

increase up to the maximum is observed for these compounds. After long CA storage slow formation of volatiles and a significantly lower maximum is obtained during ripening.

On the other hand, some compounds do not follow the evolution profile of the total sum of volatiles. An example is given in Figure 6, which shows a diminishing trend for 2-methylpropyl acetate for the different ripening periods. This can be explained by the fact that probably valine instead of a fatty acid is the precursor for the alcohol moiety of the carboxylic ester (Salunkke, 1976).

CONCLUSION

The work reported here shows that although CA storage prevents deterioration due to rotting and physiological disorder, it importantly influences the eating quality of the fruit. By means of a combination of a representative isolation of aroma compounds, quantitative high-resolution gas chromatography, and mass spectrometry, we have objectively proved that there is a significant flavor decrease for apples and a deficiency for ester production after long CA storage. If CA storage is used simply to extend storage life of a product of only average quality, apple consumption is unlikely to increase. In order to offer better quality, regulations for shorter storage periods should be established.

Registry No. Acetaldehyde, 75-07-0; 1-propanol, 71-23-8; ethyl acetate, 141-78-6; 1-butanol, 71-36-3; propyl acetate, 109-60-4; 2-methylbutanol, 137-32-6; 3-methylbutanol, 123-51-3; 2-methylpropyl acetate, 110-19-0; hexanal, 66-25-1; butyl acetate, 123-86-4; *trans*-2-hexenal, 6728-26-3; 3-methylbutyl acetate, 123-92-2; propyl butyrate, 105-66-8; butyl propionate, 590-01-2; pentyl acetate, 628-63-7; butyl butyrate, 109-21-7; hexyl acetate, 142-92-7; *cis*-3-hexenyl acetate, 3681-71-8; butyl 2-methylbutyrate, 15706-73-7; pentyl butyrate, 540-18-1; undecane, 1120-21-4; hexyl propionate, 2445-76-3; hexyl butyrate, 2639-63-6; butyl hexanoate, 626-82-4; estragole, 140-67-0; hexyl 2-methylbutyrate, 10032-15-2;

tridecane, 629-50-5; 4-methylpentyl butyrate, 83471-19-6; CO₂, 124-38-9.

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Received for review August 23, 1982. Accepted February 16, 1983. This investigation was supported by the "Instituut ter bevordering van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw". Financial support was received from the I.W.O.N.L. and furthermore the National Fonds voor Wetenschappelijk Onderzoek and the "Ministerie voor Wetenschapsbeleid".

Treatment of Golden Delicious Apples with Aldehydes and Carboxylic Acids: Effect on the Headspace Composition

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Application of vapors of C₃- to C₆-aldehydes or C₂- to C₆-carboxylic acids to intact Golden Delicious apples results in the formation of alcohols and esters. The aldehydes are either transformed into the corresponding alcohols and esterified with carboxylic acids present in the tissues or (to a small degree) oxidized into the acids, which combine with alcohols present as such, or derived from the aldehydes. Carboxylic acids yield either esters or alcohols (probably by way of the aldehydes) or smaller carboxylic acids by β -oxidation where possible, which are then in turn used as the substrate. While these additions have a great impact on the total composition of the headspace, as shown by GLC after enrichment on Tenax GC, no large or reproducible effect on the flavor of treated fruits could be demonstrated organoleptically.

Until recently there was a general trend to select high-yield apple varieties, with a good appearance, strong illness resistance, and good transport and storing properties but without paying too much attention to the flavor quality.

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With the improvement of storing technology, it is now possible to keep apples in an intact condition long after harvest. In general they suffer, however, from a loss of flavor, which depends moreover on the storing conditions (Shatat et al., 1978; Willaert et al., 1983). As part of a long-term project about the organoleptic quality of fruits and vegetables, a study was undertaken about the metabolic processes leading to the synthesis of aroma volatiles. The main substances present in the aroma of Golden

Delicious apples are esters. Their formation in fruits seems to be largely dependent on the availability of the precursor acids and alcohols (Yamashita et al., 1975, 1976, 1977; Knee and Hatfield, 1981) and, as far as the acids are concerned, on the relative amounts in which they are present (Paillard, 1979; De Pooter et al., 1981). In previous experiments, where climacteric intact Golden Delicious apples were treated with propionic acid vapors, a large effect on the volatile composition was found by GLC analysis of the headspace after enrichment on Tenax GC but, up to 11 days after addition of the acid, no reproducible changes in the taste could be detected. After about a month at room temperature, however, the treated fruits, although clearly overripe, still looked healthy, showed no necroses, and, more interestingly, evolved an intense odor, best described as synthetic ester-like (De Pooter, 1979). As it was found afterward that added propionic acid, which is probably only present in very minor amounts in Golden Delicious apples, decreased normal ester production and changed the normal ester pattern (De Pooter et al., 1981), it seemed worthwhile to repeat the above experiments extensively with acetic and butyric acids, as both substances are the major constituents of the volatile esters, and to try out the effect of pentanoic and hexanoic acids, which could at least in part be used as precursors to respectively propionic acid and butyric and acetic acids. Aldehydes were included as test substances, as they are probable metabolic intermediates between carboxylic acids and alcohols (Paillard, 1979; De Pooter et al., 1981, and references cited therein) and could have a positive influence on the aroma quality of apples by providing useful precursors.

EXPERIMENTAL SECTION

Fruits. Golden Delicious apples from the test orchards at Meerdonk (1979) and Glabbeek (1980) (Belgium) and from a commercial grower at Zottegem (1981) (Belgium) were either used directly or stored in cooled cells before use.

Application of Test Substances; Sampling and Sample Injection of the Headspace Volatiles. Apples (1.5–2 kg) were placed in desiccators (± 8 L) kept at 17 °C in a thermostat. The vessels were continuously flushed with air (150 mL/min). Test substances (100 μ L) which were sufficiently volatile at room temperature to ensure complete evaporation in 24 h (acetic, propionic, and butyric acids, propanal, butanal) were placed in a two-necked flask, installed between a compressed air cylinder and the desiccator, and carried away into the apple containers as they evaporated. The less volatile compounds (pentanoic and hexanoic acids; pentanal and hexanal) were directly injected into the incubation vessel. Before sampling, the air flow was increased to 400 mL/min so as to prevent undue accumulation of headspace volatiles and to ensure their immediate removal on elimination from the apples. After 30 min a Tenax GC 60–80-mesh tube (length 11 cm; i.d. 12 mm; 1.8 g adsorbent) was attached to the outlet of the desiccator (sample time 15 or 30 min) and the air flow was readjusted to 400 mL/min. Desorption of the headspace volatiles and concentration in a trap cooled with liquid air was performed according to a previous publication (Dirinck et al., 1981). For injection, the substances were flash-evaporated by means of a 1250-W portable flood lamp.

Experiments with Apple Disks. Apple disks (50 g), cut out of the peel (diameter 12 mm; thickness ± 2 mm), were suspended in 100 mL of phosphate buffer (0.1 M; pH 5.8) containing 1 mg of chloramphenicol and 3 mg of paraoxon [carboxyl esterase inhibitor (Sae et al., 1971; Brandt et al., 1980)]. Air was led through the suspension

at a rate of 150 mL/min, and after 1 h an emulsion of 25 mg of linoleic acid in a solution of 25 mg of Tween 80 in 5 mL of H₂O was added. Aroma samples were collected for 30-min periods after 2, 4, and 6 h on adsorption tubes (diameter 8 mm; length 75 mm; 0.8 g of Tenax GC) with an air elution rate of 150 mL/min.

Gas Chromatography. The volatiles were separated in a Varian 2700 or 3700 gas chromatograph, equipped with a flame ionization detector and a 150 m \times 0.6 mm i.d. glass column coated with SE-52. Operation conditions were as follows: linear temperature programming from 10 to 200 °C at 1 °C/min; carrier gas He, 4 mL/min; injector and detector temperature 250 °C. Identification of compounds was made by means of gas chromatography–mass spectrometry as described previously (Dirinck et al., 1981). Structures were assigned by comparison of the spectra with those of authentic, synthetic samples (De Pooter et al., 1981). Quantitative determinations were obtained by co-injection of 1 μ g of undecane and tridecane each as external standards in the adsorption tubes before desorption of the volatiles and by normalization of the values obtained from an electronic integrator (Infotronics 204) against the mean value for the alkanes. Consecutive samples showed a variation on the peak areas (or the amounts of substance present, expressed in micrograms per kilogram per 15 min in the tables) of maximum 10% (where the smaller area was taken as 100), from propyl acetate on, but a variation of up to 50% for acetaldehyde, propionaldehyde, and lower alcohols. The fluctuating trapping of the latter substances is characteristic for Tenax GC (Bertsch et al., 1974; Daelmen et al., 1975; Novotny et al., 1974).

Sensory Analyses. For sensory evaluation the triangle test (Kramer and Twigg, 1966) was applied, with a panel of 10–12 members, who performed two tests each. Panelists were asked to select the odd sample, exclusively based on apple flavor. Samples were prepared from quarters of apples, randomized before composing the test sets.

RESULTS AND DISCUSSION

Treatment with Acetic, Propionic, and Butyric Acids. A typical gas chromatogram of the volatiles of untreated Golden Delicious apples in their climacteric ripening period showing prominent peaks for butyl and hexyl acetates (Ip 819 and 1018, respectively) is depicted in Figure 1.

Full-grown, unripe fruits responded to the addition of the acids by a slight, but sustained increase in respiration (De Pooter et al., 1982) and by a higher ester production up to 5 days after treatment (Figure 2). In all three cases the latter phenomenon may be attributed to a heightened synthesis of esters derived from the added precursors during the first days (Tables I–IV). There are, however, some notable differences. On application of acetic acid much more butyl and hexyl acetate is formed than in the blank, while the concentration of the other esters increases slightly or remains constant (Tables I and II). This contrasts to the transformations induced by application of propionic or butyric acids, where the latter yield higher concentrations not only of respectively propionates and butyrates but also of propyl and butyl esters (Tables I, III, and IV). This indicates that both acids are reduced into the corresponding alcohols, probably by way of the aldehydes [cf. De Pooter et al. (1981), and references cited therein]. Added acetic acid only stimulates formation of acetates and not of ethyl esters. As in the circumstances used it is impossible to quantify acetaldehyde or ethanol in a reproducible way, one can only speculate about the lack of ethyl ester formation, although results from Knee

Table I. Ester Formation by Golden Delicious Apples on Treatment with Carboxylic Acids: Blank

esters, $\mu\text{g kg}^{-1}$ (15 min) ⁻¹	Ip-SE ₅₂	days after treatment						
		1	5	8	12	15	22	26
propyl acetate	717	0.09	0.36	1.93	3.19	4.84	4.92	5.52
2-methylpropyl acetate	782	0.20	0.19	0.42	0.23	0.34	0.15	0.25
propyl propionate	814							
butyl acetate	819	9.35	23.02	46.63	50.63	59.49	43.18	40.14
3-methylbutyl acetate	885	1.00	1.30	7.57	7.66	9.68	7.66	7.07
propyl butyrate	903		0.11	0.47	0.57	0.98	0.40	0.43
butyl propionate	911	0.31	0.97	2.82	3.17	3.47	2.79	2.23
pentyl acetate	918	0.48	0.80	1.73	1.82	1.94	1.32	1.32
butyl butyrate	1001	2.24	2.05	3.28	2.62	2.48	1.51	1.18
hexyl acetate	1018	9.57	20.31	44.22	52.40	57.10	40.17	37.87
butyl 2-methylbutyrate	1045	0.15	0.78	1.68	1.42	1.20	0.82	0.92
propyl hexanoate + butyl pentanoate + pentyl butyrate	1098 1098 1098	0.15	0.23	0.78	0.84	0.96	0.66	0.57
hexyl propionate	1108	0.34	1.26	4.42	5.98	6.16	4.83	3.77
butyl hexanoate + hexyl butyrate	1194 1196	9.75	9.11	17.46	15.52	14.99	11.20	8.59
hexyl 2-methylbutyrate	1240	0.65	3.14	8.49	7.44	7.65	6.19	4.92
hexyl pentanoate	1293	0.18	0.19	0.48	0.47	0.51	0.36	0.23
hexyl hexanoate	1390	2.87	3.06	6.95	6.21	7.21	5.46	4.00

Table II. Ester Formation by Golden Delicious Apples on Treatment with Carboxylic Acids: Acetic Acid

esters, $\mu\text{g kg}^{-1}$ (15 min) ⁻¹	days after treatment						
	1	5	8	12	15	22	26
propyl acetate	0.27	0.87	1.83	4.18	3.94	5.78	4.17
2-methylpropyl acetate	0.47	0.42	0.32	0.40	0.18	0.27	0.27
propyl propionate							
butyl acetate	26.46	36.03	46.69	52.89	45.27	47.31	31.62
3-methylbutyl acetate	1.96	5.07	7.60	9.31	8.06	8.56	5.23
propyl butyrate		0.36	0.40	0.45	0.46	0.42	0.31
butyl propionate	0.66	1.81	2.83	3.35	2.92	2.83	1.89
pentyl acetate	1.17	1.61	1.88	2.01	1.69	1.50	1.10
butyl butyrate	3.24	2.91	3.13	2.92	2.30	1.54	1.10
hexyl acetate	24.63	35.90	43.63	57.21	52.15	43.20	30.81
butyl 2-methylbutyrate	0.42	1.62	1.83	1.21	1.13	0.85	0.75
propyl hexanoate + butyl pentanoate + pentyl butyrate	0.21	0.33	0.75	0.67	0.68	0.59	0.50
hexyl propionate	0.49	2.14	4.58	6.11	5.75	4.53	3.02
butyl hexanoate + hexyl butyrate	9.91	13.18	14.81	14.58	12.24	10.18	6.94
hexyl 2-methylbutyrate	0.75	5.09	8.13	7.84	7.15	6.42	4.44
hexyl pentanoate	0.19	0.24	0.66	0.44	0.35	0.28	0.23
hexyl hexanoate	2.93	3.95	5.61	6.29	5.23	4.67	3.26

Table III. Ester Formation by Golden Delicious Apples on Treatment with Carboxylic Acids: Propionic Acid

esters, $\mu\text{g kg}^{-1}$ (15 min) ⁻¹	days after treatment						
	1	5	8	12	15	22	26
propyl acetate	1.67	2.04	3.11	3.20	3.77	4.79	4.82
2-methylpropyl acetate	0.23	0.23	0.25	0.30	0.29	0.19	0.24
propyl propionate	3.28	0.18					
butyl acetate	8.51	19.70	32.63	47.95	45.52	42.51	36.74
3-methylbutyl acetate	0.70	2.73	5.92	9.61	8.53	8.61	7.48
propyl butyrate	1.30	0.63	0.67	0.54	0.55	0.46	0.34
butyl propionate	7.56	1.77	2.19	3.05	3.02	3.21	2.51
pentyl acetate	0.93	3.11	3.28	3.12	2.33	1.81	1.45
butyl butyrate	1.80	1.78	2.17	2.70	2.34	1.99	1.59
hexyl acetate	8.40	29.47	40.41	52.96	49.21	40.47	34.94
butyl 2-methylbutyrate		1.32	1.26	1.51	1.37	1.12	1.06
propyl hexanoate + butyl pentanoate + pentyl butyrate	1.42	0.69	0.85	0.88	0.74	0.74	0.69
hexyl propionate	7.40	2.77	4.49	5.54	5.40	4.96	3.82
butyl hexanoate + hexyl butyrate	7.18	10.27	14.23	15.77	15.75	11.89	9.43
hexyl 2-methylbutyrate	0.53	4.11	8.26	9.60	9.56	7.89	6.19
hexyl pentanoate		0.51	0.73	0.72	0.55	0.42	0.33
hexyl hexanoate	1.87	3.89	5.58	6.01	5.66	4.98	3.90

and Hatfield (1981) indicate that there is a certain preference of the ester-forming enzyme system of apples for longer chain alcohols.

Comparison of the total ester production up to 5 days after addition of the carboxylic acids shows that it is highest for acetic and butyric acids and decreases from propionic acid to the blank (Figure 2). This sequence

corresponds to the normal importance of their esters in the headspace of untreated fruits and leads one to attribute also a certain selectivity of the ester-producing system of apples in the use of the carboxylic acid precursors. The composition of apple aroma would thus be determined not only by the availability of acids and their relative concentration but also by their identity. Paillard on the other

Table IV. Ester Formation by Golden Delicious Apples on Treatment with Carboxylic Acids: Butyric Acid

esters, $\mu\text{g kg}^{-1}$ (15 min) ⁻¹	days after treatment						
	1	5	8	12	15	22	26
propyl acetate	0.04	1.04	2.16	2.92	4.12	5.26	5.39
2-methylpropyl acetate	0.18	0.58	0.41	0.26	0.26	0.19	0.15
propyl propionate							
butyl acetate	10.79	27.41	44.78	46.64	43.04	43.64	38.16
3-methylbutyl acetate	0.83	5.51	9.80	8.90	8.16	8.53	7.89
propyl butyrate	0.55	0.76	0.48	0.70	0.66	0.45	0.42
butyl propionate	0.47	1.91	2.64	3.31	3.15	3.23	2.55
pentyl acetate	0.38	1.60	1.79	1.84	1.62	1.44	1.24
butyl butyrate	25.91	3.04	2.91	2.67	2.32	1.80	1.45
hexyl acetate	5.93	28.68	40.82	46.39	44.04	40.40	35.70
butyl 2-methylbutyrate	0.41	1.81	1.74	1.53	1.25	1.12	1.02
propyl hexanoate + butyl pentanoate + pentyl butyrate	0.44	0.36	0.65	0.75	0.68	0.74	0.65
hexyl propionate		1.83	4.30	5.80	5.80	5.30	4.20
butyl hexanoate + hexyl butyrate	22.03	12.83	14.14	13.04	12.49	11.56	9.27
hexyl 2-methylbutyrate	0.56	5.35	8.89	8.52	8.64	7.94	6.51
hexyl pentanoate		0.28	0.37	0.39	0.40	0.34	0.25
hexyl hexanoate	1.10	4.59	5.62	5.85	6.14	5.54	3.71

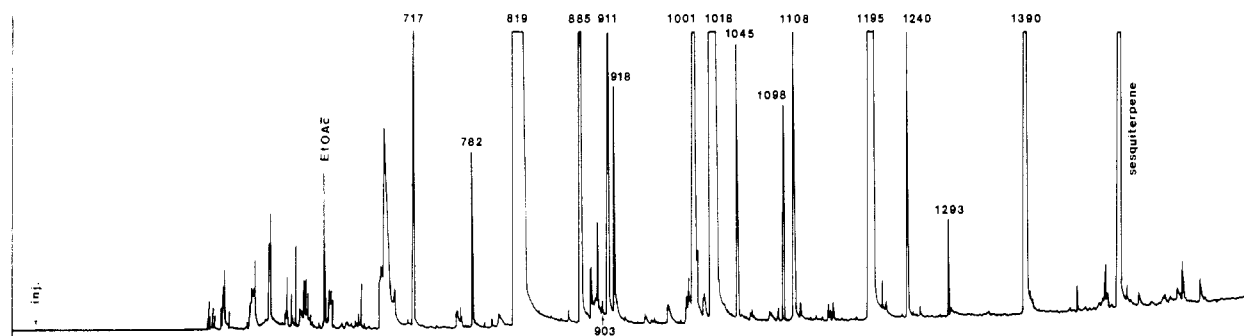


Figure 1. Representative gas chromatogram of the headspace of Golden Delicious apples. Peaks are identified by their Kováts index.

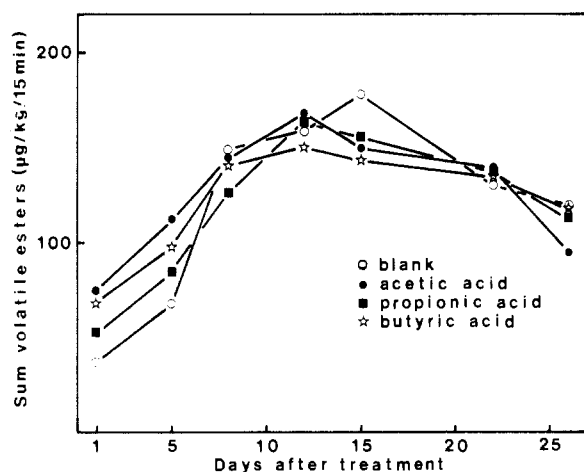


Figure 2. Ester formation by Golden Delicious apples on treatment with carboxylic acids.

hand proposes a regulating system in which formation of the needed carboxylic acids by β -oxidation would be determining (Paillard, 1979). Knee and Hatfield (1981) suggest finally, on the strength of treatments of apples and apple tissue with alcohols, that the tissue has a constant capacity for esterification of alcohol and that the ester concentration depends on the available supply of alcohols. These seemingly conflicting results and conclusions might be explained in our case by extrapolating the ripening-inducing effect which carboxylic acids have on immature preclimacteric apples (De Pooter et al., 1982) to mature apples. They could have a stimulating influence and could possibly bring the apples to a slightly further ripening stage, promoting precursor formation and esterification (Figure 2).

Treatment with Aldehydes and with Pentanoic and Hexanoic Acids. In all cases the composition of the headspace is intensely influenced by addition of the precursors. On treatment with aldehydes, the content of all esters derived from the corresponding alcohols increases strongly (Tables V and VI), confirming the activity of alcohol dehydrogenase in apple (Bartley and Hindley, 1980). Apart from this expected observation, the aldehydes are also oxidized into the corresponding acids. This phenomenon is clear with propanal and pentanal because propionates and pentanoates are absent or present in only small concentrations in the blank and is confirmed, e.g., by the greater content of propionic acid derivatives in the headspace after treatment with pentanal. Pentanoic and hexanoic acids are smoothly esterified and partly degraded by β -oxidation. But whereas pentanoic acid is still nicely transformed into the corresponding alcohol and pentyl esters, hexanoic acid seems to be much less easily reduced and leads only to a slight increase of hexyl esters. Moreover, there is a striking correspondence in the changes in composition of the headspace of apples treated with hexanal and hexanoic acid (excluding hexyl acetate, hexyl butyrate, and hexyl hexanoate). This could mean that the aldehyde might play a role in the ester formation as a precursor to hexanoic acid, itself at least in part the origin of butyric and acetic acids. It would also imply that linoleic acid (and lipoxygenase) is directly involved in the aroma ester formation sequence, as suggested in a broader sense by Mazliak (1970). As it is impossible to introduce linoleic acid into intact apples by the methods applied in the foregoing experiments, owing to its lack of volatility, apple disks were treated with the acid. As Table VII shows, the amount of most of the representative volatiles in the headspace of the treated sample after 6 h is higher than in the blank, indicating that linoleic acid may indeed be

Table V. Ester Formation by Golden Delicious Apples One Day after Treatment with Aldehydes

esters, $\mu\text{g kg}^{-1}$ (15 min) ⁻¹	blank			
	blank	propanal	blank	butanal
propyl acetate	0.38	2.74	0.36	0.40
2-methylpropyl acetate	0.52	0.30	1.27	1.25
propyl propionate		0.21		
butyl acetate	15.70	14.84	18.57	43.46
3-methylbutyl acetate	1.01	0.70	1.04	1.64
propyl butyrate		1.87	0.28	0.19
butyl propionate	0.55	2.62	0.62	1.11
pentyl acetate	0.59	1.03	0.69	0.89
butyl butyrate	3.90	3.15	3.53	10.57
hexyl acetate	15.10	17.26	12.51	18.51
butyl 2-methylbutyrate	0.37	0.29	0.54	1.10
propyl hexanoate + butyl pentanoate + pentyl butyrate	0.33	2.58	0.27	0.36
hexyl propionate	0.69	2.07	0.26	0.55
butyl hexanoate + hexyl butyrate	12.58	10.11	14.11	22.26
hexyl 2-methylbutyrate	1.30	1.45	0.73	1.39
hexyl pentanoate	0.22	0.27	0.20	0.21
hexyl hexanoate	3.11	3.20	3.52	3.83

Table VI. Comparison of Ester Formation by Golden Delicious Apples One Day after Treatment with Aldehydes and Carboxylic Acids

esters, $\mu\text{g kg}^{-1}$ (15 min) ⁻¹	blank		penta- noic acid	hexa- noic acid	blank		hexanal
	blank	pentanal			blank	hexanal	
propyl acetate	0.24	0.82	0.70	0.21	0.04	0.31	
2-methylpropyl acetate	0.76	0.89	0.93	0.69	0.52	0.44	
butyl acetate	12.52	18.33	9.77	17.03	11.53	14.48	
3-methylbutyl acetate	1.05	2.03	1.58	1.12	0.93	0.72	
propyl butyrate				0.06			
butyl propionate	0.39	0.66	1.27	0.21	0.14	0.17	
pentyl acetate	0.61	35.24	16.78	0.58	0.38	0.45	
butyl butyrate	2.72	3.44	2.88	5.82	4.49	7.77	
pentyl propionate		1.15	1.93				
hexyl acetate	8.38	12.21	4.83	10.08	9.08	29.83	
butyl 2-methylbutyrate	0.34	0.52	0.32	0.28	0.23	0.11	
propyl hexanoate + butyl pentanoate + pentyl butyrate	0.17	6.36	13.15		0.17	0.20	
hexyl propionate	0.18	0.65	1.06	0.18	0.06	0.29	
pentyl 2-methylbutyrate		0.43					
hexyl 2-methylpropionate	0.05		1.05				
butyl hexanoate + (pentyl pentanoate ?) + hexyl butyrate	6.28	10.99	16.09	12.60	6.65	23.12	
hexyl 2-methylbutyrate	0.28	0.28	0.21	0.23	0.42	0.90	
hexyl pentanoate	0.12	5.32	4.53	0.24	0.07	0.11	
hexyl hexanoate	1.47	1.13	0.80	2.22	1.59	8.91	

Table VII. Aroma Volatile Formation by Golden Delicious Apple Disks in Buffer after Addition of Linoleic Acid

aroma volatiles, $\mu\text{g 50 g}^{-1}$ (30 min) ⁻¹	blank			linoleic acid		
	after 2 h	after 4 h	after 6 h	after 2 h	after 4 h	after 6 h
	2-methylpropyl acetate	0.05	0.07	0.01	0.07	0.02
hexanal	0.18	0.10	0.09	0.39	0.26	0.35
butyl acetate	0.69	0.37	0.18	0.89	0.40	0.24
3-methylbutyl acetate	0.62	0.29	0.17	0.69	0.37	0.38
butyl propionate	0.06	0.02	0.01	0.03	0.01	0.02
pentyl acetate	0.05	0.03	0.02	0.06	0.04	0.05
butyl butyrate	0.15	0.07	0.04	0.10	0.05	0.02
hexyl acetate	1.24	0.83	0.53	1.79	1.09	0.83
hexyl propionate	0.18	0.16	0.10	0.11	0.13	0.13
butyl hexanoate + hexyl butyrate	0.68	0.56	0.42	0.50	0.53	0.55
hexyl 2-methylbutyrate	0.23	0.23	0.21	0.24	0.32	0.37
hexyl hexanoate	0.16	0.16	0.15	0.10	0.18	0.22

at least in part a precursor to aroma esters in a scheme as proposed by Eriksson (1979).

CONCLUSION

Application of aldehydes and carboxylic acids to intact climacteric apples results in an increased volatile production and, in the case of precursors with an uneven carbon chain, in a changed headspace pattern. Evaluation of the feasibility of adding precursors to apples in view of improving their aroma on storage is difficult at this moment as the late-climacteric fruits used in these experiments had a high inherent flavor, which hampered the assessment of changes in the organoleptic quality.

Moreover, the observed effects were short-lived (8 days). However, as the influence was sustained longer when early-climacteric fruits were treated (De Pooter et al., 1981), it might be that application of precursors immediately after picking and before storage might give a positive result. This possibility is now being investigated.

Registry No. Acetic acid, 64-19-7; propionic acid, 79-09-4; butyric acid, 107-92-6; propanal, 123-38-6; butanal, 123-72-8; pentanoic acid, 109-52-4; hexanoic acid, 142-62-1; pentanal, 110-62-3; hexanal, 66-25-1; propyl acetate, 109-60-4; 2-methylpropyl acetate, 110-19-0; propyl propionate, 106-36-5; butyl acetate, 123-86-4; 3-methylbutyl acetate, 123-92-2; propyl butyrate, 105-66-8; butyl propionate, 590-01-2; pentyl acetate, 628-63-7; butyl

butyrate, 109-21-7; hexyl acetate, 142-92-7; butyl 2-methylbutyrate, 15706-73-7; propyl hexanoate, 626-77-7; butyl pentanoate, 591-68-4; pentyl butyrate, 540-18-1; hexyl propionate, 2445-76-3; butyl hexanoate, 626-82-4; hexyl butyrate, 2639-63-6; hexyl 2-methylbutyrate, 10032-15-2; hexyl pentanoate, 1117-59-5; hexyl hexanoate, 6378-65-0; pentyl propionate, 624-54-4; pentyl 2-methylbutyrate, 68039-26-9; pentyl 2-methylpropionate, 2445-72-9.

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Received for review December 6, 1982. Accepted March 7, 1983. The investigations are supported by the Belgian Instituut ter bevordering van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw. The I.W.O.N.L., the Nationaal Fonds voor Wetenschappelijk Onderzoek, and the Ministerie voor Wetenschapsbeleid are thanked for financial aid.

Effect of Parboiling on Texture and Flavor Components of Cooked Rice

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Parboiling of *japonica* and *indica* rice affected the cooking properties of milled rice and resulted in a harder and less sticky texture of the cooked rice and reduced extractability of protein in the rice grain. During the parboiling process, the unbound lipid and free fatty acid in milled rice decreased, whereas the lipid bound to starch and protein and free phenolic acid increased. The results of GC analyses of the headspace volatiles of cooked rice and the steam-distilled volatiles of milled rice revealed that, after parboiling, *trans*-2-alkenals, *trans*-2,*trans*-4-decadienal, phenylacetaldehyde, and 4-vinylphenol had increased whereas 1-alkanols had decreased.

Parboiled rice has been conventionally produced by the process of presoaking, steaming, and drying with the use of rough rice. An effect of parboiling is improvement of the milling degree, and firmer and less cohesive qualities of cooked, parboiled rice were desired by people in many countries other than Japan. Consequently, parboiled rice is now produced in India, Thailand, the United States, Italy, and other countries by using modern mechanical methods. Japanese, however, prefer sticky cooked rice in general, and there is no necessity to parboil to improve the milling degree and other qualities in the case of *japonica* rice. Therefore, parboiled rice has not been commercially produced in Japan until now, and few investigations on parboiling of *japonica* rice have been reported.

Many studies concerning the changes in the rice grain resulting from parboiling have been done with the use of

indica rice samples. Subba Rao and Bhattacharya (1966) and Padua and Juliano (1974) reported the effect of parboiling on the thiamin content of rice. Bhat Sondi et al. (1980) reported the effect of processing conditions on the oil content of parboiled rice bran. Reyes et al. (1965) and Alary et al. (1977) investigated the effects of amylose on some characteristics of parboiled rice. Raghavendra Rao and Juliana (1970) investigated the effect of parboiling on some physical properties of rice, and they reported the protein fraction was less efficiently extracted from parboiled rice and the changes in amylographic characteristics on parboiling were influenced by the amylose content of the rice sample. Pillaiyar and Mohandoss (1981) reported that the cooking qualities of parboiled rice are related to the parboiling temperature, and Priestley (1976, 1977) suggested that amylose complexed with fatty acids induced by parboiling affected gelatinization and solubilization of starch.

These reports were concerned mainly with physico-chemical properties of parboiled rice, and no papers relating to the flavor of cooked, parboiled rice have been presented. This work was conducted on both parboiled *japonica* and *indica* rice samples to investigate the effect

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