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Enhancement of Aroma Volatile Compounds in Apples

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ABSTRACT

Apple aroma is a complex of volatile compounds produced by fruit. It is one of the most important quality factors giving a characteristic flavour to fruit and its products. The present study investigated the effect of short-term hypoxic concentrations and duration of CO_2 and/or N_2 treatments at 20°C on changes in production of important aroma volatile compounds after treatment during shelf-life conditions at 20°C and 70% RH, in some commercial apple cultivars at harvest and following storage in air or controlled-atmospheres (CA).

Different methods of extracting and analysing aroma volatiles from apples were compared in order to optimise a process for subsequent experiments. Juice from homogenised apple fruit could be held in an ice bath for up to 60 minutes after homogenisation without loss of major volatile compounds. Octyl acetate concentrations between 50 and 5000 ppm in the final concentrated sample was a suitable internal standard for GLC analysis; as an external standard, a mixture of authentic volatile compounds of known concentration provided accurate quantification of aroma volatiles from juice samples. Volatiles were obtained from apple juice either by a dynamic headspace (purge and trap) technique using a Tenax® trap or by direct extraction with a diethyl ether:n-pentane (2:1, v/v) mixture. The solvent extraction technique was simpler and faster than the purge and trap method, taking 5 seconds rather than 1 hour; it was also more efficient, resulting in 1.7 fold more total volatiles with better reproducibility.

Application of hypoxic gas atmosphere to apples (100% CO_2, 100% N_2 or < 2.5% O_2) demonstrated consistently enhanced headspace acetaldehyde, ethanol and ethyl acetate in 'Granny Smith', 'Braeburn' and 'Red Delicious' cultivars. A marked increased production of ethanol in response to hypoxic treatments was always followed by a several fold enhancement in both number and concentration of ethyl esters, including the aroma-impact volatiles ethyl butanoate, ethyl 2-methyl butanoate and ethyl hexanoate in juice from all cultivars. The increased concentration of these compounds

was accompanied by decreased production of other esters requiring the same acyl group for their synthesis, such as propyl butanoate, butyl acetate and hexyl acetate, and some alcohols and aldehydes, including hexan-1-ol, 2/3-methyl butan-1-ol and *trans*-2-hexenal. These results confirmed the hypothesis of the competitive nature of the acyl esterifying system in apples. Exposing apples to 100% CO_2 for 18 - 24 hours at 20°C achieved optimum enhancement; a longer time (48 hours) did not further increase important aroma-impact ethyl esters but caused a marked reduction in non-ethyl esters, while a shorter period of exposure (6 - 12 hours) had minimal effect. Apples previously stored (0°C) for 6 months or longer before exposure to hypoxic treatments did not have important volatile ethyl esters enhanced. Application of 1000 ppm ethylene for 24 hours did not increase volatile production in apples compared with non-treated fruit.

Poststorage production of most aroma volatile compounds from 'Granny Smith' and 'Fuji' apples stored in a controlled-atmosphere (CA) of 2% CO_2 + 2% O_2 at 0.5°C was depressed after 10 - 14 weeks storage, although 2-methyl butan-1-ol was enhanced and there was no effect on *trans*-2-hexenal. Poststorage treatment with 100% CO_2 (24 hours at 20°C) consistently and markedly enhanced headspace acetaldehyde, headspace ethanol, headspace ethyl acetate and aroma impact compounds, ethyl butanoate, ethyl 2-methyl butanoate and ethyl hexanoate in fruit from both refrigerated air (RA) and CA storage regimes. The hypoxic treatment had no effect on production of butan-1-ol and hexan-1-ol in CA, or hexanal in RA 'Granny Smith', propan-1-ol and butan-1-ol in either RA or CA, or hexanal and *trans*-2-hexenal in RA 'Fuji' apples. Hypoxic treatments reduced production of butyl and hexyl acetate in 'Fuji' apples, and 2-methyl butan-1-ol in both cultivars. The ability to sustain enhanced production of ethyl esters in CO_2 treated RA or CA 'Granny Smith' or CA 'Fuji' apples decreased as time of storage progressed, probably due to shortage of acyl CoA substrates for volatile synthesis. CA retarded flesh softening and acid loss in both cultivars.

Examination of volatile production from 6 commercial apple cultivars established that esters, alcohols and hydrocarbons accounted for 70% - 88% of the total number of volatiles found and compounds with straight chain and even numbered carbons predominated in the composition of esters and alcohols. Differences among apple

cultivars were associated with number and concentration of volatile compounds produced. Treatment with 100% CO_2 (24 hours at 20°C) consistently enhanced production of headspace volatiles in all cultivars. Production of aroma impact ethyl esters following hypoxic treatments consistently occurred with 'Red Delicious', 'Braeburn', 'Granny Smith' and 'Pacific Rose', with less of a response in 'Cox's Orange Pippin' and none in 'Royal Gala' apples. Non ethyl esters and alcohols, other than ethanol and propan-1-ol, were reduced after CO_2 treatment in all cultivars, except for butan-1-ol in 'Cox's Orange Pippin' apples. Hexanal and *trans*-2-hexenal were either reduced or not affected following CO_2 treatment, depending on cultivar. The magnitude of enhancement and the degree of reduction in production of aroma volatile compounds following hypoxic treatment varied among cultivars; the higher the magnitude of enhancement of ethyl acetate, the greater the degree of reduction in other acetate esters, supporting the concept of a competitive interaction in the acyl esterification in apples.

Hypoxic treatments consistently caused profound increases in aroma volatiles in most apples cultivars studied. Such a treatment has potential to increase the strength and value of commercially important flavour fractions in apple juice and aqueous essence and enhance aroma in fresh apples.

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