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RIPENING INDUCED IN PRE-CLIMACTERIC IMMATURE GOLDEN DELICIOUS APPLES BY PROPIONIC AND BUTYRIC ACIDS

HERMAN L. DE POOTER, JAN P. MONTENS, PATRICK J. DIRINCK, GUIDO A. WILLAERT and NICEAS M. SCHAMP

Laboratory of Organic Chemistry, Faculty of Agricultural Sciences, State University of Gent, Coupure 653, B-9000 Gent, Belgium

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Key Word Index—*Malus pumila*; Rosaceae; pre-climacteric apple fruit; induced ripening; propionic acid; butyric acid.

Abstract—When intact immature pre-climacteric Golden Delicious apples were treated with propionic or butyric acid vapours, ripening occurred, with attendant respiration climacteric, yellowing and aroma formation in a way almost identical to that when ethylene was used as trigger.

INTRODUCTION

During the study of aroma formation in apples aimed at improving the quality of fruits stored for a long time, precursor vapours were added to intact apples instead of employing aged discs[1] or tissue cultures[2]. When short chain carboxylic acids were applied to climacteric Golden Delicious apples a sharp increase in carbon dioxide production occurred (Fig. 1), in addition to ester formation[3]. These results differ from those obtained in analogous experiments with apple slices, where respiration remained constant[1]. As this addition of short acids to intact fruits led to a change in respiration reminiscent of that induced by ethylene treatment of pre-climacteric ones, it seemed worthwhile to investigate the effect of propionic and butyric acid vapours on pre-climacteric apples. The choice of these two precursors was dictated by their known effect on the aroma composition of Golden Delicious apples[3].

RESULTS AND DISCUSSION

The respiration of untreated fruit remained low up to day 19, when a slow increase took place (Fig. 2). In the treated fruits, however, carbon dioxide evolution started at a higher level, diminished (as is found when propylene is added to very immature pre-climacteric avocados[4]), but increases afterwards from day 8 onwards, and then showed all the characteristics of a climacteric. Attendant ripening phenomena, such as yellowing of the peel, aroma formation (Fig. 3), softening of fruit flesh and changes in the acidity–sweetness ratio occurred. None of these was found in the control until day 27. When a reference sample of pre-climacteric apples was treated with ethylene on day 7, ripening was observed. Broadly speaking, the aroma composition of the ripening apples was independent of the trigger compound used.

The analogy between the respiration curves and the aroma composition of apples treated with the two organic acids and ethylene suggests a relation in their mode of action. The latter substance influences ripening and is now thought to be derived almost

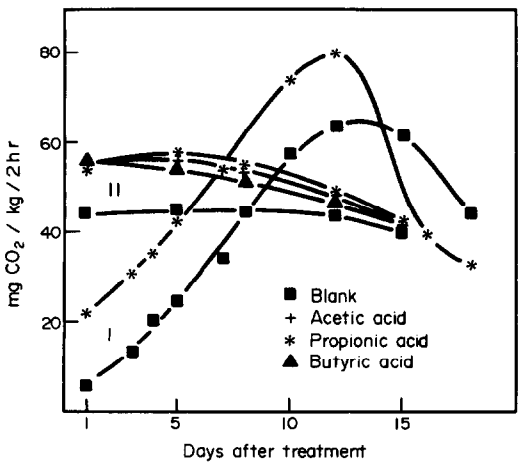

Fig. 1. Respiration of early-climacteric (I) (harvest 1979) and late-climacteric (II) (harvest 1980) Golden Delicious apples treated with organic acids.

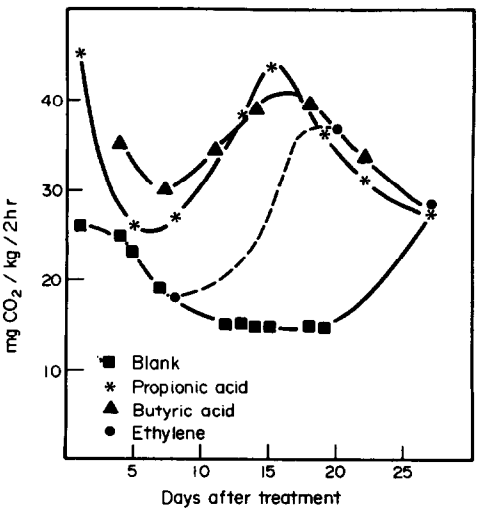

Fig. 2. Respiration of pre-climacteric Golden Delicious apples treated with organic acids. Ethylene was applied on day 7.

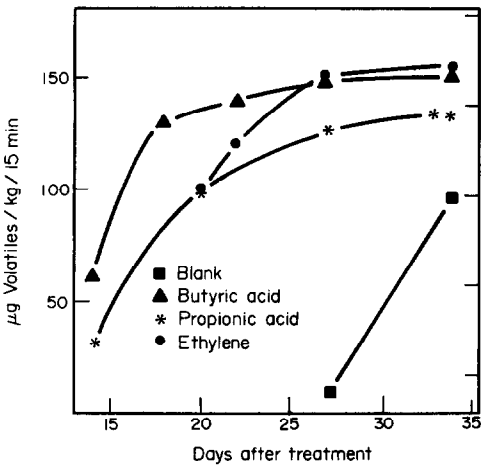

Fig. 3. Total volatile ester production by pre-climacteric Golden Delicious apples after treatment with organic acids. Ethylene was applied on day 7.

exclusively from L-methionine by way of 1-aminocyclopropane-1-carboxylic acid (ACC) ([5] and refs. therein).

$$\text{L-Met} \longrightarrow \xrightarrow{\text{ACC-synthase}} \text{ACC} \longrightarrow C_2H_4.$$

To explain the sudden surge of ethylene preceding visible ripening, Yang [5] proposes a biosynthetic sequence in which "ACC-synthase is first developed, leading to the formation and accumulation of ACC, adequate to allow the production of System 1 ethylene", which in turn may trigger high activity in the enzyme converting ACC, thus leading to the massive production of System 2 ethylene marking the onset of ripening[5].

On the other hand, Burg and Burg [6] showed [^{14}C]-ethylene formation from [2-^{14}C]propionate in apple tissue, and Shimokawa and Kasai [7] demonstrated the enzymatic nature of the transformation with banana slices and homogenate. This reaction, however, is still not generally accepted[8].

In view of our results obtained with propionic acid, it may well be that it plays a role in the ripening process. It could account for the formation of small amounts of starter "System 1 ethylene" (see above) in apples. In an analogous reaction, or by way of leaking of the β-oxidation cycle, butyric acid might well be transformed into propylene, which is known to stimulate ethylene production[4]. On the other hand, butyric acid could be transformed into acetic acid, which has been proposed as a possible precursor of ethylene[9; cf 6]. The starter alkenes would thus be formed from the same precursors needed by the fruit for the synthesis of aroma volatiles. When massive "System 2 ethylene" production then starts, circumstances are also prepared for successful aroma formation. The proposed mechanism also implies that at the moment of ethylene synthesis, catabolism is already at work. This is in accordance with results obtained by Kende and Hanson[10] from experiments with flowers of *Ipomoea tricolor*, where rolling up of rib segments (indicating loss of turgor and changes in membrane permeability) precede ethylene production.

Nevertheless, the arguments in favour of the proposed mechanism notwithstanding, we find it fitting at this stage of the investigation to make certain reservations about the general validity of the observed phenomena. The fruits were treated with relatively large amounts of acid at the start of the experiment, and although it is only partly resorbed (75–80%), and thereafter slowly eliminated (experiments with propionic acid indicated that 9 days after addition most of the compound was removed [3]), the possibility that non-physiological concentrations exaggerated the observed changes and that the surmized ethylene production was the result of a wounding-like effect may not be excluded. It is hoped that these questions may be answered by addition of smaller amounts of acid and by the use of ^{14}C-precursors.

EXPERIMENTAL

Pre-climacteric immature Golden Delicious apples (60–70 mm) were gathered on 3 September 1980 and immediately treated with 100 µl propionic or butyric acid vapours in batches of 2 kg[3]. The addition took 12–24 hr. Volatiles were concd on Tenax GC tubes and analysed as previously described[3, 11]. CO_2 was determined by transformation into $BaCO_3$, followed by treatment with excess 0.1 N HCl and titration with 0.1 N NaOH[12].

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