

DECREASED HYDROGEN SULPHIDE CONTENT IN VALENCIA ORANGES AFTER FREEZE DAMAGE

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Key Word Index—*Citrus*; Rutaceae; orange; hydrogen sulphide; fruit; freeze damage.

Abstract—The hydrogen sulphide content of headspace gases above freshly extracted Valencia orange juice from freeze-damaged and control fruit was determined. The average value for control fruit was about three times higher than that for fruit suffering moderate to heavy freeze damage, indicating a potential use as an indicator of freeze damage to fresh citrus fruit.

When citrus fruit suffers moderate freeze damage, the damage is often not visible until the fruit has been harvested and stored, where it shows poor keeping quality. Any chemical change as a result of freeze damage which could be measured would be helpful to citrus growers and processors for handling of the harvested fruit.

In an earlier study to monitor hydrogen sulphide content of juice from citrus fruit during a growing season, levels of hydrogen sulphide were found to decrease significantly in fruit subjected to a severe freeze within a week after the freeze [1]. The relatively low level of hydrogen sulphide persisted as long as the fruit remained on the tree (4 weeks). In the current study, Valencia oranges from trees that showed varying degrees of freeze damage were analysed for hydrogen sulphide content 4–5 months after a severe freeze had affected the Florida citrus crop.

The headspace gases above freshly extracted Valencia orange juice were monitored for their hydrogen sulphide content during a 1 hr period. Table 1 lists the average values for hydrogen sulphide content determined for ten samples of fruit that had suffered moderate or heavy freeze damage and for seven samples from fruit suffering only mild freeze damage (control samples). Individual hydrogen sulphide determinations were made for all samples at 2, 10, 20, 40 and 60 min after juice extraction and at 5, 30 and 50 min after extraction for some samples. As in an earlier study [1], no distinct pattern of hydrogen sulphide content with time after extraction was observed. Thus an average value gave a more meaningful result, and only the average values are reported in Table 1.

The average hydrogen sulphide level for the control fruit was more than three times that for the freeze-damaged fruit. The two averages were significantly different at greater than a 99% confidence level by the Student's *t*-test. Only one of the values for the freeze-damaged fruit was higher than the average value for the

control fruit, and one value for the control fruit was slightly lower (0.09 ppm) than the average value for the freeze-damaged fruit.

Possibly, the decreased level of hydrogen sulphide in freeze-damaged fruit is a result of mechanical damage to cells, which permits enzymic reactions to occur prior to juice extraction, such as the degradation of methionine or cysteine to hydrogen sulphide [1]. Thus juice extraction from freeze-damaged fruit would not generate as much hydrogen sulphide as when undamaged fruit is used.

Table 1. Hydrogen sulphide concentration (ppm) in juice from control and freeze-damaged* Valencia oranges

Degree of freeze damage and 1982 date harvested	Location	Average of 5–8 determinations
Mild		
21 May	BRB†	0.09
24 May	BRB	0.54
24 May	TGS‡	0.35
24 May	BRB	0.50
24 May	BRB	0.37
25 May	TGS	0.53
2 June	BRB	0.21
Average		0.37
Moderate to heavy		
24 May	TGS	0.06
24 May	TGS	0.03
24 May	BRB	0.01
25 May	TGS	0.54
25 May	TGS	0.22
26 May	BRB	0.13
2 June	BRB	0.00
2 June	BRB	0.09
2 June	BRB	0.03
2 June	BRB	0.00
Average		0.11

*Freeze occurred on 13 January 1982.

†BRB = Budwood Registration Bureau.

‡TGS = Triangle Grove Service.

*Southern Region, Agricultural Research Service, U.S. Department of Agriculture.

Evidence that the hydrogen sulphide was released during extraction and was not present in the intact fruit was obtained in this study with control fruit. Withdrawal by the procedure of Maier *et al.* [2] of 4–10 ml samples of the interior gas of several fruit and analysis by the above method showed no hydrogen sulphide present.

Thus the measurement of hydrogen sulphide content of freshly extracted citrus juice has potential as an index of quality for determining the degree of freeze damage to fresh citrus fruit. The effect of decreased hydrogen sulphide in headspace gases above freeze-damaged fruit was present several months after freeze damage had occurred.

EXPERIMENTAL

Valencia orange samples were obtained from Mr. Leon Hebb, Citrus Budwood Registration Bureau, Winter Haven, Florida, and from Triangle Grove Service, Winter Haven, Florida, and were judged for degree of freeze damage based on location and

visual damage to the trees. Virtually no fruit escaped at least mild freeze damage from the 13 January 1982 freeze (L. Hebb, personal communication). Fruit was washed, halved and the juice expressed by hand from 1–3 fruits for each sample. A 100 ml portion of fresh juice in a 125 ml Erlenmeyer flask was used for hydrogen sulphide determination with a gas chromatograph equipped with a flame photometric detector as described earlier [1, 3]. Headspace samples (10 ml) were withdrawn in the period from 2 to 60 min after extraction. Average values for 5–8 determinations for each sample are reported in Table 1.

REFERENCES

1. Shaw, P. E. and Wilson, C. W., III (1982) *J. Agric. Food Chem.* **30**, 685.
2. Maier, V. P., Brewster, L. C. and Hsu, A. C. (1973) *J. Agric. Food Chem.* **21**, 490.
3. Shaw, P. E., Ammons, J. M. and Braman, R. S. (1980) *J. Agric. Food Chem.* **28**, 778.

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VOLATILE COMPOUNDS FROM *TRITICUM AESTIVUM*

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Key Word Index—*Triticum aestivum*; Gramineae; wheat; volatiles; C₉ aldehydes and alcohols.

Abstract—Volatile compounds were isolated from aerial parts (foliage and culms) of wheat plants by reduced pressure steam distillation-extraction and identified by gas chromatography-mass spectrometry and co-chromatography with authentic compounds. Infrared spectra were also obtained on some constituents. Compounds identified included nonanal and related unsaturated C₉ aldehydes and alcohols as major components and some additional aldehydes, alcohols and a ketone.

INTRODUCTION

Volatile compounds have been extensively investigated in the edible portions of plants [1] but not as thoroughly in the remaining aerial parts of most major crops. It is known that volatile compounds are involved in plant-parasite interactions [2–6] and greater attention is now being focused on identification of members of this class of compounds in crop plants based on their possible functions in insect and pathogen interactions with plants. As part of an investigation of the volatile compounds in crop plants we have isolated and identified some volatile compounds from wheat.

RESULTS AND DISCUSSION

Approximately 2 mg of volatile oil was isolated per 1 kg of the aerial parts of wheat plants (foliage and culms). A list of compounds isolated and identified by GC/MS and

co-chromatography with authentic compounds is given in Table 1. In some instances where adequate sample was available, IR spectra were also obtained. Among the major compounds found were nonanal and a group of closely related unsaturated C₉ aldehydes and alcohols. C₉ aldehydes and alcohols were isolated and characterized as major and characteristic volatile constituents of members of the cucurbit family in earlier work and appear to contribute to their flavour chemistry [7–9]. It has been shown that nonanal and, subsequently, other volatile compounds including nonanal, octanol and 6-methyl-5-hepten-2-one stimulate germination of fungal spores including those of *Puccinia* species which parasitize wheat plants [10, 11]. Nonanal was a major volatile component and 6-methyl-5-hepten-2-one was present in spore distillates and in airstreams drawn through wheat rust (*Puccinia* species) spores [10]. There have been no reports about effects on spore germination of the unsaturated C₉