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Flavour in potatoes

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The intrinsic nutritional quality of foods counts for little if they are not acceptable to the consumer. The reasons why certain foods are more acceptable than others are extremely complex, but one of the undoubtedly more important factors is flavour. Like any other aspect of quality, the most desirable flavour for any given food will depend on a number of considerations, but in any one country there will be a norm acceptable to the majority of consumers. Changes in the flavour of a food due to genetic factors, to variations in the conditions of growth and storage, or to manufacturing processes are therefore obviously of great importance in determining the acceptability of a food. In this paper methods are described for studying such changes in the volatile substances responsible for the aroma of cooked potatoes,

and they could also be applied to other cooked foods. The potato was selected for study not only because it is an important constituent of diet, but because samples of several varieties that had been grown or stored under a number of defined controlled conditions were readily available. Potatoes suffer from the disadvantage, however, that although they are occasionally enjoyed for their own characteristic flavour when new or when prepared by baking, they are generally regarded as vegetables with a rather uninteresting weak flavour, and when boiled are best suited as a neutral background against which other foods such as roast meats and green vegetables can be appreciated. In other common methods of preparation, such as frying, roasting or mashing with butter, it is difficult to assess the significance of the flavour of the potato itself.

The flavour of cooked potatoes

Like that of any other food, the flavour of cooked potatoes is a composite of both tatse and aroma and it is only the latter property that will be considered here. It has been previously shown (Self, Rolley & Joyce, 1963) that the aroma of boiled potatoes is mainly due to a mixture of volatile compounds of relatively low boiling point ($<140°$), and that several members of this same group of volatile substances were produced from a number of other foods on boiling (Self, Casey & Swain, 1963). Differences in aroma between one cooked vegetable and another appear to be related to differences in the relative amounts of each volatile component present and variations in the rate at which they are produced. These observations, coupled with the facts that the volatile components were not conspicuously present in raw foods, and that they continued to be produced even after several hours' heating, suggested that these components were produced by the degradation of metabolites common to all biological material.

It was shown (Casey, Self & Swain, 1963*a,b*) that the majority of low-boiling volatile components from cooked potatoes can be produced in vitro by boiling solutions of amino acids with sugars and pectin. The amino acids not containing sulphur are oxidatively decarboxylated to produce aldehydes containing one fewer carbon atom (i.e. alanine gives acetaldehyde), but the sulphur-containing acids undergo more complex reactions leading to alkyl sulphides and related compounds. The reaction between amino acids and sugars and related compounds is by no means stoicheiometric; in fact probably less than $0·01\%$ of the amino acids present is transformed during the normal time of cooking (30 min). This accounts for the fact mentioned above that in vivo the production of volatile substances can continue for several hours. The rate at which the volatile components are produced in vitro is markedly affected by the nature of the reactants as well as by temperature, and in vivo, enzyme-catalysed reactions may also play a part (Kupiecki & Virtanen, 1960). Although differences in aroma between one vegetable and another or changes in aroma during the cooking of a given vegetable may be related ultimately to the amounts and nature of precursors present and to the time and temperature of cooking, with all these variables to consider it is hardly likely that the relationship will be a simple one. Nor has the connexion between the subjective evaluation of aroma and

the objective measurement of low-boiling volatile substances yet been fully investigated. Nevertheless differences in aroma may be expected with potatoes of different variety or of different age, if these contain varying quantities of the precursors. It should be stressed that these are not the only factors that may influence the aroma of potatoes; some off-flavours are undoubtedly due to the presence of uncommon volatile substances, which may be equally responsible for certain strong, but otherwise desirable aromas.

In this preliminary study, therefore, in which the volatile compounds from the boiled potato were separated and identified by capillary-column gas chromatography (Self, Land & Casey, 1963; Self, 1963), quantitative differences due to variety, maturity, growing conditions, storage and methods of cooking are reported, without relation either to their effect on aroma as such, or to the overall flavour.

Experimental

Gas chromatography. The gas-chromatographic techniques previously described in detail (Self, Land & Casey, 1963) were used with few modifications. However, as it was found that nylon capillary columns have the serious defect of selective absorption of the lower alcohols, and possibly amines, in this work stainless-steel capillary tubing was used. It was first washed through with Alkaterge T (Honeywill and Stein Ltd, Mayfair Place, London W.1) in diethyl ether (J. F. K. Huber, 1962, personal communication), to provide a smooth absorption surface on which to deposit the stationary phase, e.g. silicone oil or Polyethylene Glycol 200. Untreated columns gave much poorer separations. The columns were used in conjunction with either the small argon detector or the flame ionization detector. The separated components were identified as usual, by retention times and mixed chromatography on two phases and, whenever possible, by smell.

Sample preparation. (1) Random samples of ten potatoes, free from obvious signs of blemish or disease, were used for most of the analyses described. The potatoes were well washed in cold water to remove adhering soil, and cut in half from stem to bud end. One set of halves was kept as a control when necessary, e.g. when studying the effect of adding salt. The halves were cut into 5 mm slices and 500 g placed in 750 ml water in a 2 l. reaction vessel fitted with an all-glass water-cooled reflux condenser. The top of the condenser was closed with a rubber bung through which were passed two pieces of hypodermic needle tubing. The mixture was heated quickly to boiling by a 450 W electrothermal mantle and then maintained at gentle reflux. Samples of the vapour collected at the top of the condenser were removed, after the desired time of boiling, through one of the hypodermic tubes into an enrichment trap, consisting of a loop of nylon or stainless-steel capillary tubing immersed in liquid oxygen. The vapour sample (usually 5 ml) which contained the volatile components produced on boiling, was withdrawn with a mechanically operated syringe attached to the far side of the trap in which the volatile components were condensed. The enrichment trap afforded up to a thousandfold concentration of the volatile substances, and the sample thus obtained was in a suitable form for injection onto the capillary column.

(2) For smaller samples of potato (5 g), a system similar in principle to that above, but having a total internal volume of 15 ml, was used (small system). The flasks were heated in an oil-bath kept at $110 \pm 1°$. Usually five such systems were used together, in order to eliminate as far as possible any variations in experimental conditions. The five samples were withdrawn simultaneously into separate traps at one of nine different rates (from 0·5 to 10 min/ml). It was found essential in this small system to use antibumping beads to reduce the effect of pressure waves which otherwise tend to force volatile components in the sample straight through the trap without allowing time for condensation. The presence of water vapour in samples of large volume (>1 ml) taken from these small systems was also shown to cause errors due to its quenching effect on the chromatographic detector. Each separate system was calibrated against a solution of methanol in water (1·0 ml, 100 μg/ml) which was heated for 15 min, and a sample of the headspace vapour collected and chromatographed as described above. As a check on the calibration method, a standard solution of pectin in water (10 mg/ml) was heated for $\frac{1}{2}$ h in each apparatus and the methanol produced by the hydrolysis of pectin (Casey *et al.* 1963*b*) was collected and separated as before.

Results and discussion

The results of experiments on the calibration of ten separate sets of apparatus showed that each gave different peak heights on the recorder even when careful attention was paid to all sources of variation considered possible. However, provided the experimental conditions were rigorously adhered to, this was not a serious source of error. This conclusion is borne out by the fact that the results obtained by the two methods of calibration were in agreement, which also confirmed that it was possible to use the small system for the comparison of volatile compounds produced from vegetables on boiling.

Owing to the difficulties in calibrating the large apparatus, the results obtained for a number of the experiments in which it was used, although consistent within a group, cannot readily be compared from one experiment to another. Within any one group, however, the results are the means of values obtained in at least three separate experiments, and so any comparisons that have been made are most probably valid. At this stage in the investigation only differences in peak height of more than twofold are considered significant, and for certain components (e.g. methanol) even a fourfold difference may have no effect on aroma, since the concentration is generally too low to be detected by the nose. It may be, however, that certain components of this type do affect the subjective assessment of aroma.

Thirteen conspicuous low-boiling volatile substances are usually obtained from boiling potatoes (Self, Rolley & Joyce, 1963). Not all of these volatile compounds are present in major quantities, nor do all of them vary in any one study. In some instances composite peaks, rather than individual components, have been compared and these are shown under group numbers in the tables. The use of different stationary phases, column temperatures or flow-rates enables such composite peaks to be resolved, but it has not been considered necessary at this stage of the investigation.

Table 1. *Comparison of four varieties of potato on reaching maturity*

	Group no. of volatile substances						
Variety	1	2	3	4	5	6	7
Majestic	55	33	29	2	41	0	78
Doon Star	17	18	41	3	30	0	100
King Edward	47	50	65	5	66	1	150
Arran Viking	11	6	8	3	35	0	130

Group composition: 1, hydrogen sulphide and methanethiol; 2, acetaldehyde; 3, dimethyl sulphide; 4, unknown; 5, acetone, 2-methylpropanal and propanal; 6, 2- and 3-methylbutanal; 7, methanol.

The values given in all tables are effective peak heights obtained by gas chromatography. The results shown in Table 1 were obtained with potatoes grown at one centre and lifted in early August, and indicate that, at this time, the particular stock of Arran Viking might be expected to be less highly flavoured than the rest (but cf. new potatoes, Table 2), whereas King Edward have larger amounts of the sulphur-containing volatile substances which at this concentration combine to give a more or less desirable flavour of cooked vegetables. The attractive flavour of new potatoes, however, must be due to some other cause, since, as can be seen from Table 2, the new potatoes contain much less of these sulphur-containing volatiles than the previous season's tubers. It may be that the twofold differences in diacetyl, which has a pleasant butter-like odour, or changes in certain higher-boiling components are more important factors, or indeed absence of flavour may be a desirable subjective characteristic.

Table 2. *Comparison of old- and new-season potatoes in June 1962*

	Group no. of volatile substances							
	1	2	3	4	5	6	7	8
Old (1961)	51	76	23	90	56	5	1	10
New (1962)	0	30	0	40	1	1	2	0

Group composition: 1, hydrogen sulphide; 2, acetaldehyde; 3, methanethiol; 4, acetone and propanal; 5, dimethyl sulphide; 6, 2-methylpropanal; 7, diacetyl; 8, 2- and 3-methylbutanal.

The effect of storage is shown in Table 3. Because of the observations made previously about comparisons between one experiment and another carried out at different times, not too much stress should be laid on the absolute differences found on storage, but more on the relative change of pattern. Thus, whereas the newly lifted tubers produced no measurable quantities of ethanol, or 2- or 3-methylbutanal, these were all present in the old potatoes, along with much higher quantities of all the other volatile components with the exception of methanol.

The effect of the type of soil in which the potatoes were grown on the volatile components produced on boiling was less marked, as shown by the results in Table 4. However, such differences may be more significant in certain other varieties, or after storage. It would certainly be expected that such differences would exist in view of the known effect of soil type on the nitrogen content of tubers (Schwimmer & Burr, 1959).

Table 3.   *Effect of 6 months' storage on potatoes (Majestic)*

	Group no. of volatile substances							
	1	2	3	4	5	6	7	8
Before	55	33	29	2	41	0	78	0
After	>100	>100	90	12	60	18	12	27

Group composition: 1, hydrogen sulphide and methanethiol; 2, acetaldehyde; 3, dimethyl sulphide and ethanethiol; 4, unknown; 5, acetone, 2-methylpropanal and propanal; 6, 2- and 3-methylbutanal; 7, methanol; 8, ethanol.

Table 4.   *Comparison of Arran Viking potatoes grown at two centres*

Centre	Group no. of volatile substances						
	1	2	3	4	5	6	7
Isle of Ely (Fen)	20	5	15	0	14	0	200
Cambridge (Sandy loam)	13	18	10	1	41	0	150

Group composition: 1, hydrogen sulphide and methanethiol; 2, acetaldehyde; 3, dimethyl sulphide and ethanethiol; 4, unknown; 5, acetone, 2-methylpropanal and propanal; 6, 2- and 3-methylbutanal; 7, methanol.

The removal of peel on the other hand appeared to make some difference to the amount of volatile substances produced (Table 5); for example the two- to three-fold increase in dimethyl sulphide from the unpeeled as compared with peeled potato would be expected to give an overall increase in the aroma. The effect of salt was rather unexpected since Bassette, Özeris & Whitnah (1962) have reported that the addition of salts (e.g. Na_2SO_4) increases the amount of volatile substances obtained from model systems. It is possible, however, that sodium chloride may depress the chemical transformations which produce such volatile components in the potato.

Table 5.   *Effect of removing the peel from potatoes and of adding salt*

Treatment	Group no. of volatile substances										
	1	2	3	4	5	6	7	8	9	10	11
Unpeeled	2	14	88	30	63	—	26	11	16	6	—
Peeled	15	16	93	73	25	9	54	83	38	8	—
Unpeeled: alone	30	100	100	94	90	10	42	15	12	9	27
salt added	2	79	80	(80)		1	23	17	14	20	7

Group composition: 1, hydrogen sulphide; 2, methanethiol; 3, acetaldehyde; 4, unknown; 5, dimethyl sulphide; 6, unknown; 7, 2-methylpropanal; 8, acetone; 9, 2- and 3-methylbutanal; 10, methanol; 11, ethanol.

Besides the experiments reported, the difference between boiled and baked potatoes has been investigated. It was observed that there was an overall increase in the total quantities of volatile components produced from potatoes on baking, especially in the amounts of 2- and 3-methylbutanal. This effect could be explained simply as an acceleration in the rate of production of these volatile substances from their precursors (leucine and isoleucine) at the elevated temperature of baking.

Finally it might be mentioned that the relatively weak flavour which is usually obtained when so-called instant mashed potato products are made according to the manufacturers' instructions (e.g. by adding hot water or hot milk) is probably due to the fact that the degradative reactions leading to the volatile constituents of flavour only occur weakly, if at all. This observation and the experiments with baked potatoes support the suggestion that the desirable aroma of cooked foods is due to such degradative reactions.

Conclusions

The results reported are to be regarded as exploratory and only comparative within each group, and the observed differences are not necessarily true for all varieties of potato. Nevertheless, the following points have been established.

(1)   There are distinct differences in the flavour volatile components between the potato varieties so far examined.

(2)   New potatoes are notable for their lower concentrations of volatile substances rather than for the appearance of characteristic different constituents.

(3)   The effect of storage is markedly to alter the flavour 'spectrum'.

(4)   The soil types in which the potatoes are grown appear to affect the volatile substances produced but much more work will be necessary to explore this effect.

(5)   Simple alterations in cooking procedures may produce marked changes in the flavours produced.

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The environment for chemical change in dried and frozen foods

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The primary object of the main methods of food preservation is to maintain the food in a wholesome condition during prolonged periods of storage. Ideally the storage life of the food should be unlimited, a goal which can only be achieved if it is possible to attain absolute stability. Though some types of change may in particular instances be considered desirable, conditions that permit them to occur