Volatile Chemicals Identified in Fresh and Cooked Breadfruit

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Volatile constituents of fresh and cooked breadfruit were extracted with dichloromethane and identified by gas chromatography (GC) and gas chromatography/mass spectrometry. Alcohols were the major components of fresh breadfruit, and acetates were the major components of cooked breadfruit. Among 40 compounds identified in fresh breadfruit volatiles, the main constituent was *cis*-3-hexenol, which comprised 35.8% of the total GC peak areas. Among 43 chemicals identified in cooked breadfruit, the major component was ethyl acetate, which comprised 37.9% of the total GC peak areas. An extract from fresh breadfruit had a strong green note, and one from cooked breadfruit possessed cooked yamlike flavor.

INTRODUCTION

Breadfruit (Artocarpus altilis), which is native to the Pacific islands, is a large, round, starchy fruit borne by a tree. Breadfruit became widely known through Charles Nordhoff and James Hall's 1932 book, Mutiny on the Bounty, which was the basis of three movies. It is the story of the voyage of the British armed transport Bounty, which sailed to the island of Tahiti in the Great South Sea in 1787–1789 to collect a cargo of young breadfruit trees for transportation to the West Indies, where, it was hoped, the trees would thrive and eventually provide an abundance of cheap food for the slaves of the English planters.

Consumption of breadfruit has so far been limited primarily to the inhabitants of the islands of the South Pacific. It is eaten either fresh or cooked. Although many people in other parts of the world have heard of breadfruit, few have eaten it.

Breadfruit is rich in carbohydrates and proteins (Tumaalii and Wootton, 1988; Graham and Negron de Bravo, 1981). In particular, the seed of African breadfruit (*Treculia africana Decne*) has a high lipid content (Ekpenyong, 1985). Even though breadfruit is a rich source of nutrients, its use is limited because of the poor storage properties of the fresh fruit. Nochera and Caldwell (1992) studied the possible use of flour obtained from breadfruit so that local people could decrease their dependence on imported wheat. They found that bread containing 10%breadfruit flour and 5% whey and biscuits containing 10%breadfruit flour and 5% soy protein were judged most acceptable in flavor, color, and texture. Until now, however, there has been no report on the volatile constituents of either fresh or cooked breadfruit.

In the present study, volatile constituents of both fresh and cooked breadfruit were isolated and identified.

EXPERIMENTAL PROCEDURES

Materials. Breadfruit (A. altilis) was collected at Oahu, HI. Authentic reference compounds were kindly donated by Takata Koryo Inc., Ltd. (Osaka, Japan). Sample Preparation. After removal of the core and skin, breadfruit flesh was cut into approximately 1-cm cubes (total weight, 1 kg) and homogenized with 600 mL of water and 200 mL of saturated NaCl solution. Solid materials were first filtered off with a cheese cloth and then with a filter paper. The filtrate (950 mL) was extracted with 75 mL of dichloromethane using a liquid-liquid continuous extractor for 7 h. The solvent of extract was removed by distillation with a Vigreux column. The solvent of concentrated extract was further removed under a nitrogen stream until the weight became 480 mg.

For a cooked fruit sample, an unpeeled whole fruit was placed in boiling water for 10 min. The cooked fruit was treated as described above, and 520 mg of concentrated sample was obtained.

Instrumental Analyses of Volatiles. All samples were analyzed with Kovats gas chromatographic retention index I(Kovats, 1965) and gas chromatography/mass spectrometry (GC/ MS). The gas chromatographic retention index and MS fragmentation pattern of each component were compared with those of the authentic compound for qualitative analysis. A Shimadzu Model 9A gas chromatograph (GC) equipped with a 30 m \times 0.25 mm i.d. DB-Wax bonded-phase fused-silica capillary column (J&W Scientific, Folsom, CA) and a flame ionization detector (FID) was used for routine analysis. The oven temperature was held at 40 °C for 5 min and then programmed to 200 °C at 2 °C/min. The injector and detector temperatures were 250 °C. The injector split ratio was 30:1. The linear helium carrier gas flow rate was 30 cm/s.

A Varian 3500 GC equipped with a 30 m \times 0.25 mm i.d. DB-Wax bonded-phase fused-silica capillary column (J&W Scientific) and interfaced to a Finnigan MAT Model 800 ion trap detector equipped with an INCOS MS data system (Finnigan, San Jose, CA) was used for MS identification of the GC components. The oven conditions for GC/MS were held at 50 °C for 2 min and then programmed to 200 °C at 2 °C/min.

RESULTS AND DISCUSSION

The yields of total volatiles (relative to the breadfruit flesh used) were approximately 0.00003% (w/w) from both cooked and fresh breadfruit. Table 1 shows the compounds identified in fresh and cooked samples along with their GC peak area percent. Compounds are listed in the effluent order from a DB-Wax column. Among 91 peaks in the GC of a sample from cooked breadfruit, 43 compounds were positively identified. Among 73 peaks in the GC of a sample from fresh breadfruit, 40 compounds were positively identified. Although authentic chemicals of 3-hexene-2,5-diol (*E* and *Z*) were not available to conform identification, their mass spectra precisely

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 Table 1. Volatile Chemicals Identified in Fresh and

 Cooked Breadfruit

		GC peak area % ^b	
compound	Iª	cooked	fresh
methyl acetate	825	0.054	с
ethyl acetate	887	37.9	с
2-butanone	905	с	0.26
ethanol	944	16.0	с
2-pentanone	975	с	1.32
chloroform	1021	0.23	0.064
toluene	1036	0.07	C 10
ethyl butyrate	1037	C 0.070	0.16
1-methylbutyl acetate hexanal	$\begin{array}{c} 1075\\ 1078 \end{array}$	$0.072 \\ 0.054$	$\stackrel{c}{0.182}$
trans-2-pentenal and 2-pentanol	1127	0.034 0.274	0.182
2-methyl-4-pentenal	1141	0.274 C	0.305
butanol	1150	c	0.101
1-penten-3-ol	1165	0.463	0.845
2-heptanone	1178	0.478	0.429
cis-2-hexenal	1193	0.27	0.287
isoamyl alcohol	1198	0.097	c
trans-2-hexenal	1207	0.124	2.61
amyl alcohol	1256	0.07	с
hexyl acetate	1272	0.055	с
3-hydroxy-2-butanone	1277	4.85	23.3
2-ethenyl-2-butenal (tentative)	1293	0.551	0.108
cis-3-hexenyl acetate	1314	1.42	С
cyclopentanol	1323	0.472	1.48
2-heptanol	1327	0.089	0.241
hexanol	1359	0.447	2.58
trans-3-hexenol	1367	0.583	0.541
cis-3-hexenol trans-2-hexenol	1387	10.1	35.8
2-cyclohexenone	$\begin{array}{c} 1407 \\ 1412 \end{array}$	$0.128 \\ 1.35$	$0.878 \\ 0.671$
1-octen-3-ol	1412	0.45	0.391
2-cyclohexenol	1466	0.182	0.001 C
trans, trans-2,4-heptadienal	1479	c	0.086
3-cyclohexenol	1484	0.045	сс
benzaldehyde	1500	0.127	с
ethyl 3-hydroxybutyrate	1512	0.038	0.056
2,3-butanediol	1542	0.151	0.811
γ -valerolactone	1600	0.733	0.197
diethylene glycol monoethyl ether	1615	0.215	0.382
butyric acid	1625	с	0.252
trans-2(or 4)-chlorocyclohexanol	1636	2.57	1.41
ethyl benzoate	1650	0.087	C
cyclohexyl benzene	1643	С	0.067
2-methylbutyric acid	1668	C 0.026	0.287
γ -hexalactone benzyl acetate	$\begin{array}{c} 1682 \\ 1714 \end{array}$	$\begin{array}{c} 0.036 \\ 0.314 \end{array}$	С
5-ethyl-2(5H)-furanone	1734	0.098	$^{c}_{0.052}$
hexanoic acid	1844	0.102	0.641
benzyl alcohol	1867	2.71	0.084
3-hexene-2,5-diol (tentative)	1940	0.548	c
trans-3-hexenoic acid	1957	c	0.322
1,2-cyclohexanediol	1960	1.96	1.55
3-hexene-2,5-diol (tentative)	2027	0.132	с
phenylpropyl alcohol	2037	0.062	0.075
octanoic acid	2063	0.21	0.166
ethyl palmitate	2258	С	0.079
β,β -dimethylbenzenepropionic acid	2262	0.187	с
cinnamic alcohol	2274	0.232	0.039
vanillin	2531	0.068	с
			C

^a Kovats index on DB-Wax. ^b Solvent peak is excluded. ^c Not detected.

matched those of the computer library. They are, therefore, listed as tentatively identified in Table 1. Chloroform and trans-2(or 4)-chlorocyclohexanol, the chlorinatedcompounds found in the extracts, may be solvent contaminants.

In fresh breadfruit, the major volatile constituents were cis-3-hexenol (35.8%), 3-hydroxy-2-butanone (23.3%), 1,2cyclohexanediol (1.55%), and 2-pentanone (1.32%). In cooked breadfruit, the major volatile constituents were ethyl acetate (37.9%), ethanol (16.0%), cis-3-hexenol (10.1%), and 3-hydroxy-2-butanone (4.85%). Alcohols comprised 45.5% of the total volatiles identified in fresh breadfruit, while esters comprised 40% of the total volatiles found in cooked breadfruit. Fresh breadfruit has a strong green note due to cis-3-hexenol; this, however, is considerably decreased in cooked breadfruit. It is not well understood how ethyl acetate is produced by cooking, but it may be associated with the formation of ethanol, which is the second major constituent (after ethyl acetate) of cooked breadfruit. No acetates were found in a sample of fresh fruit, whereas in a sample of cooked fruit ethyl acetate, methyl acetate, 1-methylbutyl acetate, hexyl acetate, cis-3-hexenyl acetate, and benzyl acetate were detected. Acetic acid, which is a precursor of acetates, was not detected in either fresh or cooked breadfruit. Acetic acid may not be extracted due to its high solubility in water.

It is surprising that no terpenes were detected in any of the samples. One should not, however, conclude that breadfruit oil does not contain terpenes. Because there is no other report on the volatiles in breadfruit, a more detailed analysis of this oil is in order.

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