

Combined Gas Chromatography–Mass Spectrometric Analysis of the Aroma Components of Cooked Taro (*Colocasia esculenta* L.)

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ABSTRACT

Using established procedures, volatile components of taro were analysed for the first time. A total of 62 components (c. 95% of the isolate) was positively identified, and a further component (c. 2.3%) was partially characterised. Many of the identified components were classic volatile products deriving from aspecific oxidation/degradation. others were common volatiles deriving from the action of heat on amino acids and/or sugars. The most abundant component was octane (21.10%), and pyridine was present at the unusually high level of 18.60%.

INTRODUCTION

Taro (*Colocasia esculenta* L.)—also known colloquially and regionally in various parts of the world as eddo, dasheen or old cocoyam—is a member of the family Araceae and, as such, is one of the most important edible aroids (Harrison *et al.*, 1975; Bradbury & Holloway, 1988). It is an ancient crop, originating in Asia, probably in India, and then taken to Egypt where it was an important food 2000 years ago (Bradbury & Holloway, 1988). In prehistoric times, its cultivation also spread to the Pacific islands and later to the Mediterranean area and to Africa, reaching there about 100 BC. From West Africa, the crop spread to the West Indies and to tropical parts of the Americas (Chandra, 1986). It is now grown as an important subsistence root

crop, and eaten as a staple because of its high starch and energy content (Wills *et al.*, 1983; Bradbury & Holloway, 1988). It is one of the most widespread of all root crops, being grown to some extent throughout the humid tropics as a prestigious food. There are two varietal types: *Colocasia esculenta* var. *esculenta*, which produces a large edible corm with a few suckers or cormels, and *Colocasia esculenta* var. *antiquorum*, which has a small- or medium-sized corm and a large number of small edible cormels (Bradbury & Holloway, 1988).

A characteristic feature of certain cultivars is the problem of varying degrees of acidity (common to other aroids) which is removed by cooking (Bradbury & Holloway, 1988). This has been attributed partly to the presence of calcium oxalate raphides in idioblast cells and partly to an unidentified component on the surface of active raphides (Moy *et al.*, 1979; Bradbury & Holloway, 1988; Holloway *et al.*, 1989). The cooked corms have a relatively bland flavour somewhat reminiscent of cooked potatoes and cooked cereals.

Analysis of the volatile components of taro (*Colocasia esculenta* L.) has not been published hitherto. This paper therefore reports the results of the first such analysis.

MATERIALS AND METHODS

Fresh taro (*Colocasia esculenta* var. *antiquorum*) cormels were purchased from a local supermarket supplied by Geest Industries, Spalding, Lincs, and imported into the UK from the West Indies.

Isolation of volatile components

Washed taro (1 kg), cut into *c.* 2 cm cubes, in distilled water (400 ml), were extracted for 3 h in a modified (MacLeod & Cave, 1975) Likens and Nickerson (1964) apparatus using triply distilled 2-methylbutane (20 ml). Four extractions were performed and the extracts combined before low temperature-high vacuum concentration (MacLeod & Coppock, 1976) to 200 μ l at 2.6×10^{-3} kPa. A blank isolate was obtained as above, using distilled water only in the extraction flask.

Capillary gas chromatography

Both polar and non-polar capillary columns were used under the following conditions: (a) 25 m \times 0.32 mm i.d. fused silica capillary column coated with BP20 bonded phase (0.5 μ m film); helium, 2 ml/min; temperature pro-

gramme, 60°C for 10 min then 2°C/min to 200°C; detector (fid) and injector heaters, 225°C; injection volume, typically 1 µl at 25:1 split and attenuation 1 × 64, i.e. 32×10^{-11} A fsd. (b) 60 m × 0.32 mm i.d. fused silica capillary column coated with DB5 bonded phase (1 µm film); temperature programme, 40°C for 5 min then 2°C/min to 225°C; detector (fid) and injector heaters, 250°C; other parameters as for the BP20 column.

Combined gas chromatography-mass spectrometry

A Kratos MS25 instrument was used, linked on-line to a Kratos DS55S data processing system. Capillary GC conditions as above were used for both polar and non-polar columns. Injection volume was 2 µl at 25:1 split. Significant operating parameters of the MS were: ionisation voltage, 70 eV; ionisation current, 100 µA; source temperature, 200°C; accelerating voltage, 2 kV; resolution, 600; scan speed, 1 s/decade (repetitive throughout run).

Quantitative assessment

Duplicate analyses were performed. Quantitative data were derived from the TIC monitor obtained during GC-MS and, for trace components, by extrapolation from integrator (Hewlett-Packard 3370B) data obtained from the GC-FID chromatogram recorded during routine GC.

RESULTS AND DISCUSSION

Fresh taro (*Colocasia esculenta* var. *antiquorum*) cormels were purchased from a local supermarket. Aroma extracts were prepared and validated using well established procedures (Likens & Nickerson, 1964; MacLeod & Cave, 1975). The odour of the extract was representative of the cooked taro, and was described as buttery, earthy, musty/mouldy and possessing odour notes reminiscent of boiled/baked potatoes, cooked rice and roasted cereal. Four extractions were performed, and the replicate extracts were combined before concentration by high vacuum-low temperature distillation (MacLeod & Coppock, 1976). The resultant isolate, on appropriate dilution, possessed a strong aroma which was defined using the same odour qualities as described above for the extract.

Isolates were analysed by capillary GC and combined GC-MS, and the results are given in Tables 1 and 2. Fused silica capillary GC columns were used, containing either bonded-phase BP20 or DB5. Best resolution was achieved using the BP20 column, and most of the aroma components were identified using this phase (Table 1); however, a few components were

TABLE 1
Volatile Components of Taro (BP20 Column GC-MS)

Component and ref. MS (lit.) ^a	R _t (min)	Kováts index (lit.) ^b	RA ^c (%)
Diethyl ether ^d	1.05	590	TR
Hexane ^d	1.05	600	TR
Octane ^d	1.32	800	21.10
Adimethylcyclohexane	1.48		2.30
Methylpropanal ^d	1.65	800	TR
2-Methylbutanal	1.81		6.20
3-Methylbutanal	2.35	937	0.60
Butanedione ^d (i.e. diacetyl)	2.35	963	TR
2-Methylbutan-2-ol	2.73	987	0.30
2-Methylbut-3-en-2-ol	3.05	1016 ^e	1.70
Toluene	3.05	1001 ^f	TR
Pentane-2,3-dione ^d	3.43	1044	0.50
Hexanal ^d	3.81	1084	2.00
2(or 3)-Methylthiophen	3.98	1123 (2-Me)	0.20
N-Methylpyrrole	5.29	1139	0.30
Pyridine	7.02	1180	18.60
3-Methylbutan-1-ol ^d	8.05	1184	0.30
2-Pentylfuran ^d	9.13	1229	0.20
Pentan-1-ol ^d	10.72	1213	0.20
Hexan-1-ol ^d	17.57	1316	0.20
(Z)-Hex-3-en-1-ol ^d	19.41	1351	0.20
Nonan-2-one ^d	19.69	1377	0.09
Nonanal ^d	19.79	1382	0.20
Oct-1-en-3-ol ^d	23.92	1420	0.20
2-Furaldehyde ^d (i.e. furfural)	24.30	1449	0.80
Decan-2-one ^d	26.33	1480	0.10
Decanal ^d	26.51	1485	0.09
Benzaldehyde ^d	27.27	1502	0.50
Linalool ^d	30.21	1506	0.10
3,5,5-Trimethylcyclohex-2-enone	31.78		0.02
2-Acetylthiazole ^d	34.94	1639	1.80
Phenylacetaldehyde	35.26	1646	0.40
Thiophen-2(or 3)-carboxaldehyde ^d	36.73	1702 ^h (2-)	0.04
Thiophen-3(or 2)-carboxaldehyde ^d	37.54		0.05
2,6-Di- <i>tert</i> -butyl-4-methylphenol (i.e. BHT)	50.15	1870 ^f	0.09
Benzothiazole	51.09	1873 ^f	0.08
5-Methyl-2-phenylhex-2-enal	57.95		0.40
γ-Decalactone ^d	58.38	2101	0.02
δ-Decalactone ^d	59.90	2144	0.09
2-Methoxy-4-vinylphenol ⁱ (i.e. <i>p</i> -vinylguaiacol)	63.66	2160 ⁱ	1.90
Nonanoic acid	66.86	2200 ⁱ	2.10
Diethyl phthalate ^d	71.38	2303	0.10
2,3-Dihydrobenzofuran	72.15		0.30

TABLE 1—*contd.*

<i>Component and ref. MS (lit.)^a</i>	<i>R_t</i> (min)	<i>Kováts index</i> (lit.) ^b	<i>RA^c</i> (%)
Hexadecan-1-ol	72.42	~ 2 320	2.40
Indole ^d	73.56	2 351	0.20
Tetracosane	76.52	2 400	2.00
Di-(2-methylpropyl) phthalate	78.67		1.00
Pentacosane	80.73	2 500	5.60
Dibutyl phthalate	85.67	2 630 ^f	6.20
Octadecanoic acid	109.64		3.20
Eicosanoic acid	121.06		11.20

^aMS lit., *Eight Peak Index of Mass Spectra* (1983) when not cited.

^bKováts index lit., Jennings and Shibamoto (1980) when not cited—for PEG 20M—confirming general elution sequence.

^cRA, relative abundance; <0.01% quoted as trace (TR); 0.01–0.10% quoted to nearest 0.01%; >0.10% quoted to nearest 0.10%.

^dLit., Jennings and Shibamoto (1980).

^eLit., Engel and Tressl (1983).

^fLit., Yamaguchi and Shibamoto (1981).

^gLit., Mussinan and Walradt (1974).

^hLit., Stoll *et al.* (1967).

ⁱLit., Buttery *et al.* (1981).

identified only from the DB5 column (Table 2). Literature Kováts retention indices (Stoll *et al.*, 1967; Jennings & Shibamoto, 1980; Buttery *et al.*, 1981; Yamaguchi & Shibamoto, 1981; Engel & Tressl, 1983) of most components are also included in the tables, and confirm the general elution sequence. Where positive identities are given, the mass spectra obtained on GC-MS agreed with those in the literature (Mussinan & Walradt, 1974; Jennings & Shibamoto, 1980; Buttery *et al.*, 1981; *Eight Peak Index of Mass Spectra*, 1983).

A total of 62 volatile components (comprising *c.* 95% of the isolate) were positively identified, and one further component (a dimethylcyclohexane; 2.3%) was partially characterised. In comparison with many other fruits and vegetables, this is a relatively small number of aroma components, and is probably explained—at least partially—by the fact that the chemical composition of taro consists largely of water (*c.* 70%) and starch (*c.* 25%) (Wills *et al.*, 1983; Chandra, 1986; Bradbury & Holloway, 1988).

Aliphatic hydrocarbons accounted for as high a level as 29.29% of the aroma volatiles—the main representatives being the straight chain alkanes (C₆, C₈, C_{18–21}, C₂₄, C₂₅), some branched alkanes (C₈) and the straight chain alk-1-enes (C₁₉, C₂₀, C₂₄). In particular, octane was present to the extent of 21.10% of the extract. Aliphatic acids were also dominant as a

TABLE 2
Additional Volatile Components of Taro (DB5 Column GC-MS)

<i>Component and ref. MS (lit.)^a</i>	<i>R_t</i> <i>(min)</i>	<i>Kováts index</i> <i>(lit.)^b</i>	<i>RA^c</i> <i>(%)</i>
Cyclohexane	11·11	677	TR
2-Methylheptane	21·27		0·02
2,3-Dimethylhexane	21·43		TR
2,4-Dimethylhexane	21·92		0·10
Octadecane ^d	97·06	1 800	0·05
Nonadec-1-ene	102·11		0·02
Nonadecane ^d	103·09	1 900	0·05
Eicos-1-ene	108·52		0·05
Eicosane ^d	111·02	2 000	0·10
Heneicosane ^d	121·08	2 100	0·10
Octadeca-9,12-dienoic acid (i.e. linoleic acid)	126·73		0·50
Tetracos-1-ene	178·45		0·10

^aMS lit., *Eight Peak Index of Mass Spectra* (1983) when not cited.

^bKováts index lit., Jennings and Shibamoto (1980) when not cited—for nearest stationary phase (OV 101)—confirming general elution sequence.

^cRA, relative abundance; <0·01% quoted as trace (TR); 0·01–0·10% quoted to nearest 0·01%; >0·10% quoted to nearest 0·10%.

^dLit., Jennings and Shibamoto (1980).

class. They represented 17·00% of the aroma volatiles, and this was largely due to eicosanoic acid (11·20%); the other members detected were nonanoic acid (2·10%), octadecanoic acid (3·20%) and octadeca-9,12-dienoic acid, i.e. linoleic acid (0·50%). A third quantitatively significant class was the aliphatic alcohols, contributing 5·5% of the volatiles. Seven representatives were detected, namely 2-methylbutan-2-ol (0·30%), 2-methylbut-3-en-2-ol (1·7%), 3-methylbutan-1-ol (0·30%), pentan-1-ol (0·20%), hexan-1-ol (0·20%), (*Z*)-hex-3-en-1-ol (i.e. 'leaf alcohol') (0·20%), oct-1-en-3-ol (i.e. 'mushroom alcohol') (0·20%) and hexadecan-1-ol (2·40%).

The above-mentioned aliphatic hydrocarbons, acids and alcohols are classic volatile products deriving from lipid oxidation/degradation (Grosch, 1982). Also present in the taro volatiles was a number of other well known lipid-derived components, e.g. hexanal (2·00%), nonanal (0·20%), decanal (0·09%), nonan-2-one (0·09%), decan-2-one (0·10%), 2-pentylfuran (0·20%), γ -decalactone (0·02%), δ -decalactone (0·09%) and benzaldehyde (0·50%). Clearly, therefore, the lipids of taro (only 0·1–0·4%; Wills *et al.*, 1983; Bradbury & Holloway, 1988) are significant aroma precursors, and their decomposition can be by autoxidation or enzyme catalysis or else by oxidative/non-oxidative thermal degradation.

A small number of the identified volatiles derives from non-lipid precursors. The amino acid profile of taro has been reported (Bradbury & Holloway, 1988) and, for example, Strecker degradation of valine, leucine, isoleucine and phenylalanine explains the formation of methylpropanal (trace), 3-methylbutanal (0.60%), 2-methylbutanal (6.20%) and phenylacetaldehyde (0.40%), respectively. Degradation of sugars in taro (glucose 0.4%, fructose 0.4%, sucrose 0.1%, maltose 0.1%; Wills *et al.*, 1983) will account for the generation of butanedione (trace), pentane-2,3-dione (0.50%) and small amounts of furanoid compounds (other than 2-pentylfuran). The Maillard reaction explains the generation of several heterocyclic compounds, namely the furanoids, thiophenoids, thiazoles and pyrroles. A notable feature is the identification of pyridine at the extraordinarily high level of 18.60%. Although often identified in a range of different foods of plant and animal origin, it is usually present in trace amounts. It can derive from Maillard reactions, e.g. from heated glucose/cysteine or cystine (Kato *et al.*, 1973), but, with regard to the large amount present, there would appear to be an additional source for it in taro which is difficult to define from the currently published compositional data (Wills *et al.*, 1983; Bradbury & Holloway, 1988). Most of the Maillard reaction products identified are present at low concentrations, which is in keeping with the low protein and sugar contents (both *c.* 1%; Wills *et al.*, 1983; Bradbury & Holloway, 1988) of taro. It also has a low amylase content, which means that no significant breakdown of starch to maltose occurs during cooking; this latter reaction does occur in sweet potato—another root crop staple. 2-Methoxy-4-vinylphenol (1.90%) is a thermal degradation product of ferulic acid (Fiddler *et al.*, 1967; Greuell, 1974), and linalool (0.10%) is likely to be a natural metabolite. Three phthalate esters were identified, at least two of which are known contaminants from plasticisers used in packaging films.

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