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VOLATILE FLAVOUR COMPONENTS OF CASHEW 'APPLE' (*ANACARDIUM OCCIDENTALE*)

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Key Word Index—*Anacardium occidentale*; Anacardiaceae; cashew 'apple'; aroma volatiles.

Abstract—An essence of fresh cashew 'apple', obtained by well-established procedures and possessing the characteristic aroma of that fruit, was analysed by GC and by GC/MS using both EI and CI techniques. The fruit produced a very small quantity of aroma volatiles (*ca* 3.6 μg/kg fresh fruit), much less than that obtained from most similar tropical fruits. Five aldehydes comprised *ca* 26% of the sample, but terpene hydrocarbons (*ca* 38%) provided the major group of compounds, consisting of four monoterpenes (*ca* 34%) and three sesquiterpenes (*ca* 4%). Important constituents of the essence included hexanal, car-3-ene, limonene, *trans*-hex-2-enal and benzaldehyde. Car-3-ene (24.3%) was the major constituent, and it was observed that during some recent analyses of tropical fruits this relatively uncommon aroma volatile had been identified in three out of four fruits studied of Venezuelan origin.

INTRODUCTION

Anacardium occidentale is a medium-sized tropical tree indigenous to Brazil, which is now extensively cultivated in India and eastern Africa, often in large plantations. The tree survives a wide range of ecological conditions and has the virtue of growing well in rather drier areas than most other economically important trees. The important product is the cashew nut, and world production is in the region of 0.5×10^6 tonnes/year [1]. However, the tree also yields the so-called cashew 'apple', which is also edible. The fruit of *A. occidentale* is unusual, consisting of the large fleshy 'apple' below which (directly attached) hangs the true fruit, a single nut, the kernel of which is the edible cashew nut. In some countries, for example in South America, cashew 'apple' is a popular fruit, but it is not often eaten raw because of a high level of astringency, and normally it is consumed after cooking when it has an extremely pleasant and characteristic flavour. It is a very juicy, fibrous fruit which is green when raw but which turns yellow or red on ripening. It is larger than the average apple, and the flesh obviously contains no nut or seeds.

In comparison with the nut, cashew 'apple' is almost completely neglected in commercial terms, although it is, of course, available in far greater tonnage, and there is considerable potential for its development and exploitation. Its properties have been studied for many years, particularly in India, and a number of processes have been developed for converting the 'apple' into various products such as juices, jams, syrups, chutney and various beverages. However, to date no study of the nature of the volatile flavour components of cashew 'apple' has been reported, and this paper describes the results of the first such investigation.

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RESULTS AND DISCUSSION

Valid aroma concentrates of fresh cashew 'apples' from Venezuela were obtained using previously described methods [2], and constituents were identified as far as possible by GC/MS using both electron impact ionization and chemical ionization techniques. Table 1 lists the volatile components of fresh cashew 'apple', together with GC retention data, quantitative data and odour qualities of the various GC peaks. In all instances where positive indentities are given, mass spectra agreed well with those in the literature. All spectra have been published previously ([3] for monoterpene hydrocarbons, [4] for sesquiterpene hydrocarbons, [5] for many other aroma components), so need not be reported here. Literature ([5, 6]) R_t of some important components are also included in Table 1, and it can be seen that in all instances these are of appropriate value and confirm the general elution sequence. In the few cases where no odour quality is given in Table 1 this was either due to none being detected or to a minor GC peak being incompletely resolved from an adjacent larger peak such that no distinctly different odour could be perceived.

The quantitative data in Table 1 show that in total *ca* 3.6 μg of aroma components were obtained per kg of fresh fruit. This is a very low concentration, and in previous analyses of other tropical fruits using similar techniques the following range of concentrations has been determined: wood apple (*Feronia limonia*), 80 mg/kg [7]; soursop (*Anona muricata*), 1.2 mg/kg [2]; guava (*Psidium guajava*), 200 μg/kg [8]; mango (*Mangifera indica*), 60 μg/kg [9]; sapodilla (*Achras*

Table 1. Volatile flavour components of cashew 'apples' (*Anacardium occidentale*)

Peak no.	Component	RR_t (min)	R_t (literature)*	% rel. abundance	μg/kg 'apple'	Odour quality
1	Branched C_8 hydrocarbon	3.9	—	tr	tr	—
2	Methylcyclohexane plus branched C_8 hydrocarbon	4.5	—	3.1	0.11	—
3	Octane	5.1	800	2.9	0.10	—
4	A dimethylcyclohexane	5.4	—	2.2	0.08	—
5	Ethyl acetate	6.2	872	0.3	0.01	—
6	Ethylcyclohexane	6.8	—	0.3	0.01	Green, stale
7	3-Methylbutanal	7.2	937	2.5	0.09	—
8	Unknown	10.5	—	0.3	0.01	Fruity
9	Toluene	10.9	1055	3.3	0.12	Fruity
10	Unknown	11.4	—	tr	tr	Unpleasant, rancid
11	Hexanal	11.8	1084	8.4	0.30	Green grass, hexanal
12	Unknown	12.1	—	tr	tr	Very sweet, fruity
13	*m*- And/or *p*-xylene	13.1	1145	0.7	0.03	—
14	Car-3-ene	13.9	1165	24.3	0.88	Fruity, sickly
15	α-Phellandrene	14.5	1177	0.7	0.03	Estery
16	*o*-Xylene	14.8	1191	tr	tr	
17	Limonene plus *trans*-hex-2-enal	15.0	1206 1207	11.0	0.40	Green, grass
18	Unknown	15.3	—	0.5	0.02	Oily, fatty, slightly rancid
19	α-Terpinene	16.4	1239	3.7	0.13	Fruity
20	2-Methylpentan-1-ol	17.0	1268	4.5	0.16	Nutty
21	*cis*-Hex-3-en-1-ol	17.6	1351	3.1	0.11	Green
22	Unknown	17.9	—	tr	tr	—
23	Nonanal	18.3	1382	5.2	0.19	Floral, fragrant
24	Ethyl octanoate	19.0	1423	0.4	0.01	Nutty, hazelnuts
25	Unknown	19.4	—	tr	tr	Oily, stale
26	Furfural	19.9	1449	8.7	0.31	Smokey, cold meat fat
27	A dichlorobenzene	20.1	—	tr	tr	—
28	Hydrocarbon	20.6	—	tr	tr	—
29	Unsaturated hydrocarbon plus a dichlorobenzene	21.3	—	1.4	0.05	Floral, fragrant
30	Benzaldehyde	21.8	1502	3.6	0.13	Fresh green nuts, cashew
31	Unknown	22.7	—	tr	tr	—
32	*trans*-Non-2-enal	23.2	1540	0.8	0.03	Oily, fatty, linseed oil-like
33	A decanone plus a methyl ester	24.4	—	0.4	0.01	Slightly roasted cereal
34	Caryophyllene	25.1	1618	2.5	0.09	Sickly sweet, floral, fragrant
35	Acetophenone plus phenylacetaldehyde	25.9	1627 1646	0.8	0.03	Floral, fragrant, wallflower
36	Unknown	26.5	—	tr	tr	Nutty, oily, fatty
37	? Heptadecane	27.2	(1700)	0.6	0.02	Unpleasant, musty, oily, stale
38	Sesquiterpene	28.3	—	0.3	0.01	
39	Unknown	30.6	—	tr	tr	Sweet, hay
40	α-Selinene	32.7	1780	0.9	0.03	Green, hay
41	Hydrocarbon	35.5	—	2.4	0.09	Flat, dull

tr, trace.
*Refs. [5] and [6].

sapota), 5 μg/kg [10]; mangosteen (*Garcinia mangostana*), 3 μg/kg [11]. Thus cashew 'apple' liberated only slightly greater amounts of total volatiles than the very delicately flavoured mangosteen, and indeed the fruit does have a weak flavour.

Table 1 shows that the cashew 'apple' essence contained 46 main components, of which 25 (comprising *ca* 92% of the sample) were positively identified, with a further 12 (*ca* 7%) partially or tentatively characterized. The compounds identified cover a range of compound-types, although terpene hydrocarbons (*ca* 38%) provided the major group. However, five aldehydes were also detected in the sample which together comprised *ca* 26%, and this is a relatively high concentration in fruit aroma volatiles for this class of compound. Important specific components of the essence on the basis of concentration and/or odour qualities (Table 1) include hexanal, car-

3-ene, limonene, *trans*-hex-2-enal and benzaldehyde. Taking into account their common biogenesis, it is not surprising that *cis*-hex-3-en-1-ol (*ca* 3%) was also identified in the sample, as well as *trans*-hex-2-enal.

The group of terpene hydrocarbons in the cashew 'apple' essence consisted of four monoterpenes (*ca* 34%) and three sesquiterpenes (*ca* 4%). No other terpenes (e.g. oxygenated derivatives) were detected. Of the monoterpenes, car-3-ene was the major contributor (24.3%) and indeed it was the major component of the essence. This is a little surprising in that it is not one of the more common terpene aroma volatiles, although it has been previously detected in various spices and in tomato, currant, passion fruit and citrus fruits in general [12]. Furthermore, it might also seem surprising that we have claimed identification of this relatively uncommon aroma component in a number of our recent analyses of tropical fruits. Thus, we reported high levels (*ca* 26%) of car-3-ene in the aroma volatiles of mango [9] and lesser amounts (1.5%) in sapodilla fruit [10]. However, as in these previous instances, there is little doubt concerning the identification of car-3-ene in cashew 'apple' volatiles, although it is appropriate to review the evidence. First, although the mass spectra of some monoterpene hydrocarbons are very similar, the spectrum of the suspected car-3-ene from cashew 'apple' agreed very well with that in the literature [3]. The only other possibilities with similar spectra (*cis*- and *trans*-β-ocimene and α-pinene) showed a poorer match on detailed comparison of spectra. Secondly, the accurately determined R_t of the suspected car-3-ene GC peak (peak 14) of the cashew 'apple' sample was 1162 (reference standards, hexanal and *trans*-hex-2-enal). This value agrees well with the known R_t of car-3-ene under similar GC conditions (1165), whereas the R_t of the other possibilities on the basis of mass spectral evidence are very different (α-pinene, 1039; *cis*-β-ocimene, 1228; *trans*-β-ocimene, 1250). Taken together, these data provide strong evidence that peak 14 of the cashew 'apple' sample was due to car-3-ene. Similar evidence was obtained with respect to its reported occurrence in the aroma volatiles of mango [9] and sapodilla [10]. It is worth commenting that similar verification was applied to other terpene components for which mass spectral evidence was not entirely conclusive. For example, the determined R_t of the suspected caryophyllene GC peak of the cashew 'apple' sample (peak 34) was 1609 (reference standards, benzaldehyde and acetophenone). The published value is 1618, determined under the same GC conditions [6].

It is interesting to note that in our recent analyses of the aroma volatiles of nine tropical fruits only three, all from Venezuela: mango, spodilla and cashew 'apple', were shown to produce the relatively uncommon car-3-ene in their aroma volatiles. In the case of guava [8] which was also from Venezuela, the presence of a relatively large amount of myrcene (R_t 1156) in the sample could have obscured evidence of car-3-ene. It is not possible to draw any deductions from such a limited survey, but the observation is intriguing, and particularly so when it is considered that in no previous analysis of fresh mango fruit (always of Indian origin) has car-3-ene ever been detected amongst volatiles [9].

During the previous analyses of tropical fruits [2, 7–11, 13], esters or terpenes have been shown to be the major quantitative contributors to the aroma volatiles, but generally one or other of the groups of compounds has predominated. Thus, for example, soursop and guava produced, respectively, 80% and 55% of esters [2, 8], whilst mango provided 68% terpenes [9]. Cashew 'apple' is a slight exception in producing a relatively large proportion of aldehydes (*ca* 26%), but terpenes as a group still provided the major contribution to the aroma volatiles, and only 0.7% of esters were detected.

From the results reported in Table 1 it is not possible to make any positive deductions concerning which compounds might be particularly important with regard to the characteristic cashew 'apple' flavour, although clearly benzaldehyde may make a relevant contribution in this respect.

EXPERIMENTAL

Fresh cashew fruits were transported by air from Venezuela such that they could be analysed almost immediately on arrival in their ripe state. Nuts were detached from the 'apples' and were discarded.

Sample preparation. Fruit pulp (690 g) was mixed with H_2O (400 ml) and extracted for 4 hr in a Likens and Nickerson [14] apparatus as modified by MacLeod and Cave [15] using 2-methylbutane (25 ml) as solvent. At the end of this time the residue did not possess any appreciable aroma. The extract was concd to 0.25 ml as previously described [15], and the resultant essence possessed an aroma which was very similar to that of fresh cashew 'apples'.

GC. Essences were examined by FID GC using a 5.5 m × 4 mm i.d. glass column packed with 10% Carbowax 20 M coated on 100–120 BSS mesh acid-washed Diatomite C. Using an N_2 flow rate of 60 ml/min the temp. programme was 60° for 5 min followed by an increase at 12°/min to 185°. Detector and injection point heaters were at 250°.

GC/MS. A Kratos MS 25 was used, linked on-line to a Kratos DS 50S data processing system. The same GC conditions as above were used but with He (40 ml/min) as carrier gas. The single-stage, all-glass jet separator was at 250°. Both EIMS and CIMS were performed. Significant operating parameters of the MS during EIMS were: ionization voltage, 70 eV; ionization current, 100 μA; source temp., 230°; accelerating voltage, 1.5 kV; resolution, 900; scan speed, 1 sec/decade (repetitive throughout run). Identical conditions were employed during CIMS except for: reagent gas, methane; ionization potential, 100–110 eV; emission current, 5 mA.

Quantitative assessment. Samples were prepared in such a manner that a known aliquot of the fruit sample was analysed. Quantitative data were then obtained mainly from the TIC trace during GC/MS, but also from the GC FID trace for minor components. Known amounts of a selection of identified compounds (EtOAc, hexanal, *cis*-hex-3-en-1-ol and benzaldehyde) were injected under the same analytical conditions in order to enable calculation of absolute amounts of components in the essence.

Odour assessment. Aromas of the separated components of the essence were assessed at an odour port following GC. An outlet splitter at 10:1 diverted the major fraction of the eluent through a heated line to the outside of the GC oven for aroma assessment by three subjects, two of whom were familiar with cashew 'apple' flavour.

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