# VOLATILE FLAVOUR COMPONENTS OF MANGO FRUIT

ALEXANDER J. MACLEOD and NOLA GONZALEZ DE TROCONIS\*

Department of Chemistry, Queen Elizabeth College (University of London), Campden Hill Road, London W8 7AH, U.K.

(Received 30 October 1981)

Key Word Index-Mangifera indica; Anacardiaceae; mango; aroma volatiles.

Abstract—An essence of fresh Venezuelan mango fruit obtained by well-established procedures possessed the characteristic aroma of the fruit. It was analysed by GC/MS using both EI and CI. The fruit produced a relatively small quantity of aroma volatiles (ca 60  $\mu$ g/kg fresh fruit), less than that obtained from many similar tropical fruits. Terpene hydrocarbons comprised ca 68% of the sample, eight monoterpenes contributing ca 54% and four sesquiterpenes contributing ca 14%. Important constituents included  $\alpha$ -pinene, car-3-ene, limonene,  $\gamma$ -terpinene,  $\alpha$ -humulene,  $\beta$ -selinene, acetophenone, benzaldehyde and a dimethylstyrene. Car-3-ene (26%) was the major constituent, and on odour evaluation of separated components at an odour port during GC, the peak due to this compound was described as having an aroma of mango leaves. This compound has not previously been detected among mango volatiles. The only other component providing mango aroma was a dimethylstyrene, and this too is a new mango volatile.

#### INTRODUCTION

Mango (Mangifera indica L.) is one of the most popular and best known tropical fruits. It is most widely grown in India but it is also planted in almost every tropical country and sometimes rather beyond (e.g. Florida, Egypt). The fruit is medium sized (weighing on average between ca 200 and 800 g) with a green skin which turns yellow or slightly red when ripe. The skin is not consumed and underneath is a luscious, edible flesh which surrounds the central seed (stone). The fruits, which are fairly sweet, are mainly eaten fresh but they are also made into preserves and juices. The unripe fruits are used to make mango chutney. Since mango does not ship well, it is sometimes canned, often as a puree.

Despite the obvious importance and popularity of the fruit, little attention has been devoted to studying the volatile aroma components responsible for its characteristic and attractive flavour. Understandably, most such work has been carried out in India, and Gholap and Bandyopadhyay have published a number of papers on the flavour of fresh mango (e.g. refs. [1-4]). However, their first preliminary report on this subject was a verbal presentation by Angelini et al. in 1973 [5]. In 1974, Hunter et al. [6] published a detailed survey of the aroma volatiles of canned mango puree. A wide range of compounds was identified, including esters, lactones, mono- and sesquiterpenes and two interesting furanones. Monoterpene hydrocarbons (cis-ocimene,  $\alpha$ - and  $\beta$ -pinene, myrcene and limonene) seem to be particularly important contributors to the flavour of fresh. Indian mango [4], with either cis-ocimene or myrcene being the characteristic aroma compounds of green mango, depending on the variety [3]. It has been suggested that the ratio of palmitic to palmitoleic acid determines the flavour quality of the ripe fruit, a ratio of less than one resulting in strong aroma and flavour [2].

Bearing in mind the very widespread importance of mango, it was considered appropriate to study further the aroma volatiles of the fresh, ripe fruit. This paper describes the results of such a study on fruits grown commercially in Venezuela.

#### RESULTS AND DISCUSSION

Valid aroma concentrates of fresh mango fruit were obtained using previously described methods [7], and constituents were identified as far as possible by GC/EI-MS and GC/CI-MS.

Table 1 lists the volatile components of fresh mango, together with GC retention data, quantitative data and odour qualities of the various peaks. In all instances where positive identities are given, the mass spectra agreed with those in the literature. All spectra have been published previously, so none need be reported here. Kováts retention indices [8, 9] of some important components are also included in Table 1 and they confirm the general elution sequence.

The quantitative data in Table 1 show that in total ca 60 µg of aroma components were obtained per kg fresh fruit (excluding skin). This is a relatively low concentration, and in our previous analyses of other tropical fruits, using similar techniques, the following range of concentrations has been determined: wood apple (Feronia limonia), 80 mg/kg [10]; soursop (Anona muricata), 1.2 mg/kg [7]; guava (Psidium guajava), 200 µg/kg [11]; sapodilla (Achras sapota), 5 µg/kg [12]; mangosteen (Garcinia mangostana), 3 µg/kg [13]. Thus the very strongly flavoured wood

<sup>\*</sup>Present address: Bioanalysis School, Faculty of Medicine, Zulia University, Maracaibo, Venezuela.

Table 1. Volatile flavour components of mango fruit\*

Peak No.	Component	$R_t(\min)$	Kováts index (lit.)	Rel. abund. %	Amount (µg/kg fruit)	Odour quality
1	Unknown	3.5		tr†	tr	None
2	Dimethyl sulphide	4.5		tr	tr	Sulphurous, cabbage-like
3	Methylcyclohexane plus					
	branched C <sub>8</sub> -hydrocarbon	4.8	_	0.5	0.31	None
4	Octane	5.0	800	0.1	0.06	None
5	A dimethylcyclohexane	5.3		tr	tr	None
6	Unknown	6.3	_	0.1	0.06	None
7	Unknown	8.7		0.1	0.06	Slightly fruity
8	Trichloroethylene	10.0		0.7	0.43	Slightly fruity
9	α-Pinene	10.2	1039	8.2	5.01	Fragrant, scented, floral
10	Toluene	10.4	1055	tr	tr	Buttery, caramel
11	Car-3-ene	13.0	1165	26.0	15.88	Green, pungent, mango leaves
12	$\alpha$ -Phellandrene + $C_4$ -alkylbenzene	13.4	1177	0.5	0.31	Estery
13	Limonene	13.9	1206	6.0	3,67	Lemon-like
14	$\beta$ -Phellandrene	14.3	1216	2.7	1.65	Fatty, oily
15	cis-Ocimene + C <sub>4</sub> -alkylbenzene	15.0	1228	2.6	1.59	Fragrant, herbal
16	y-Terpinene	15.7	1251	7.7	4.70	Flat, dull
17	p-Cymene	16.2	1272	1.3	0.79	Herbal, slightly minty
18	A dimethylstyrene	18.6		6.2	3.79	Mango
19	Furfural	19.0	1449	13.0	7.94	Cold meat, gravy
20	Acetylfuran	20.2	1491	0.1	0.06	Green, resinous, woody
21	Benzaldehyde	21.1	1502	1.2	0.73	Wood bark, green twigs
22	5-Methyl-2-furfural	22.0	1563	0.2	0.12	‡
23	Caryophyllene	23.5	1618	0.5	0.31	Floral, fragrant
24	Acetophenone + phenylacetaldehyde	24.6	1627 1646	5.5	3.36	Sweet, floral, wallflowers
25	α-Humulene	25.8	1682	4.5	2.75	Floral, fragrant
26	Benzenoid compound	26.9		0.2	0.12	Unpleasant floral
27	Unknown	27.5		0.5	0.31	None
28	? Valencene	28.1	(1725)	0.2	0.12	Floral, green
29	β-Selinene	29.5	1730	8.7	5.31	Floral, nutty, almonds
30	Unknown	32.5		tr	tr	None
31	A methylpropenylbenzene	35.7		1.6	0.98	Sickly, cereal-like, hay
32	Hydrocarbon	41.4	_	0.5	0.31	Sweet, fruity
33	Hydrocarbon	44.2		0.2	0.12	Sweet, fruity
34	Unknown	44.7		0.3	0.18	None

<sup>\*</sup>Two samples of mango fruit volatiles were prepared and separately analysed. Each sample was examined twice by EI-MS and once by CI-MS. Quantitative data are averages (variation  $ca \pm 5\%$ ). Odour qualities were determined in replicate runs by three assessors, acting independently. The table is a composite of all data thus obtained.

apple yielded ca 1300 times the concentration of volatiles compared with mango.

Table 1 shows that mango essence contained 38 main components, of which 22 (comprising ca 89% of the sample) were positively identified, with a further 10 (ca 10%) partially or tentatively characterized. The compounds identified cover a relatively limited range of chemical classes, terpenes (ca 68%) dominating the sample. Despite previous reports [4,6], no esters or lactones were detected, and, taking into account their characteristic mass spectra, there seems little doubt that no such compounds were produced in our sample above the level of ca 0.05  $\mu$ g/kg. Important

specific compounds in the essence on the basis of concentration and/or odour qualities include  $\alpha$ -pinene, car-3-ene, limonene,  $\gamma$ -terpinene,  $\alpha$ -humulene,  $\beta$ -selinene, acetophenone, benzaldehyde and the dimethylstyrene.

Eight monoterpene hydrocarbons comprising over 54% of the sample were positively identified in the mango essence. Of these, car-3-ene was the major contributor (26%). This has not previously been reported in mango, but there was no doubt concerning its identification. It had a retention time appropriate for its known Kováts index (1165), and, although the Kováts index of myrcene (1156), which

<sup>†</sup>Trace

<sup>‡</sup>Not assessed because GC peak incompletely resolved from adjacent larger peak.

has previously been identified in mango [3, 4, 6], is very similar, the mass spectra of the two compounds are quite different [14]. In addition to its high relative abundance, the GC peak due to car-3-ene was described as having a characteristic aroma of mango leaves. Clearly it is an important contributor to mango fruit flavour, and it may be that this compound is typical of the fruit grown in Venezuela rather than in India. Car-3-ene is not one of the more common terpene aroma volatiles, although it has been previously detected in various spices and in tomato, blackcurrant, passion fruit and citrus fruits in general [15]. In addition, we recently identified it in small amounts in the aroma volatiles of sapodilla fruit [12].

The majority of the monoterpene hydrocarbons which had previously been identified in mango volatiles [3, 4, 6] were also identified in our sample, but in addition  $\alpha$ - and  $\beta$ -phellandrene were detected as well as car-3-ene.

Of the four identified sesquiterpene hydrocarbons, which made up nearly 14% of the mango essence,  $\beta$ -selinene (8.7%) was the major contributor. This too has not previously been reported among mango volatiles, but again there was no doubt concerning its identity both on the basis of appropriate retention behaviour [8] and on the basis of a good mass spectrum which agreed perfectly with that in the lit. [16]. The only two previously identified [6] sesquiterpene hydrocarbons (caryophyllene and  $\alpha$ -humulene) were also identified in our sample.

Hunter et al. [6] identified many additional compounds in canned mango puree, but it is possible that many of these originated during processing. In particular, the interesting 2,5 - dimethyl - 4 - methoxy - 2(H)furan - 3 - one (which is closely related to the 4-hydroxy-analogue which has been found in many natural sources including strawberry and pineapple) may be an artefact, since the 4-hydroxy compound has also been found in products from browning processes [6]. The same argument could apply to the other identified furanone, 2,5-dimethyl-2(H)furan-3-one [6]. Nevertheless, specific searches were made for these compounds (which have characteristic mass spectra) in our samples, but without success.

On assessment at an odour port during GC, two peaks were described as possessing significant mango character. Car-3-ene has already been discussed. The other GC peak was due to the partially characterized dimethylstyrene. Although styrene itself has often been reported among volatiles [15], derivatives are comparatively rare and certainly they have not previously been detected in mango. From the mass spectrum the compound was a dimethylstyrene, but the positions of the methyl groups, although nuclear, could not be assigned. Presumably this compound also contributes especially to fresh mango fruit flavour.

## EXPERIMENTAL

Fresh mango fruits were transported by air from Venezuela so that they could be analysed almost immediately on arrival in their ripe state. Over-ripe fruits were rejected.

Sample preparation. After removal of the stone, fruit pulp (600 g) was mixed with  $H_2O$  (400 ml) and extracted for

3 hr in a Likens and Nickerson apparatus [17] as modified by MacLeod and Cave [18], 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 0.75 ml as previously described [18]. The resultant essence possessed a strong aroma, characteristic of fresh mango.

GC. FID-GC:  $5.5 \text{ m} \times 4 \text{ mm}$  glass column packed with 10% Carbowax 20M coated on 100–120 BSS mesh acid-washed Diatomite C;  $N_2$  60 ml/min; temp. programme  $60^\circ$  for 5 min, followed by an increase at  $12^\circ$ /min to  $180^\circ$ ; detector and injection point heaters  $250^\circ$ .

GC/MS. A Kratos MS 25 instrument was used, linked on-line to a Kratos DS-50 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 EI-MS and CI-MS were performed. Significant operating parameters of the MS during EI-MS were: ionization voltage, 70 eV; ionization current, 100  $\mu$ A; source temp. 230°; accelerating voltage, 1.5 kV; resolution, 900; scan speed, 1 sec/decade (repetitive throughout run). Identical conditions were employed during CI-MS except for: reagent gas, CH<sub>4</sub>; 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 derived both from the TIC trace during GC/MS, and from the GC-FID trace. Known amounts of a selection of identified compounds (limonene, p-cymene, furfural 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, all of whom were familiar with mango aroma.

Acknowledgements—We thank Mr. W. G. Gunn and Mr. A. E. Cakebread for running the GC/MS, and Dr. G. MacLeod and Miss M. Elahee for assistance in odour assessments.

### REFERENCES

- Gholap, A. S. and Bandyopadhyay, C. (1975) J. Food Sci. Technol. 12, 262.
- Gholap, A. S. and Bandyopadhyay, C. (1976) Indian Food Packer 30, 63.
- Gholap, A. S. and Bandyopadhyay, C. (1977) J. Sci., Food Agric. 28, 885.
- Bandyopadhyay, C. and Gholap, A. S. (1979) Proc. First Indian Convention of Food Scientists and Technologists
- Angelini, P., Bandyopadhyay, C., Rao, B. Y. K., Gholap, A. S. and Bazinet, M. L. (1973) 33rd Annu. Meet. Inst. Food Technol. Paper No. 366.
- Hunter, G. L. K., Bucek, W. A. and Radfort, T. (1974) J. Food Sci. 39, 900.
- MacLeod, A. J. and Pieris, N. M. (1981) J. Agric. Food Chem. 29, 488.
- Andersen, N. H. and Falcone, M. S. (1969) J. Chromatogr. 44, 52.
- Jennings, W. and Shibamoto, T. (1980) Qualitative Analysis of Flavour and Fragrance Volatiles by Glass Capillary Gas Chromatography. Academic Press, New York.

- MacLeod, A. J. and Pieris, N. M. (1981) J. Agric. Food Chem. 29, 49.
- MacLeod, A. J. and de Troconis, N. G. (1982) Phytochemistry 21, 1339.
- 12. MacLeod, A. J. and de Troconis, N. G. (1982) J. Agric. Food Chem. (in press).
- MacLeod, A. J. and Pieris, N. M. (1982) Phytochemistry 21, 117.
- Ryhage, R. and von Sydow, E. (1963) Acta Chem. Scand. 17, 2025.
- van Straten, S. and de Vrijer, F. (1973) Lists of Volatile Compounds in Foods. 3rd edn. Central Institute for Nutrition and Food Research TNO, Zeist, Netherlands.
- Moshonas, M. G. and Lund, E. D. (1970) Flavour Ind. 1, 375
- 17. Likens, S. T. and Nickerson, G. B. (1964) Proc. Am. Soc. Brew. Chem. 5.
- MacLeod, A. J. and Cave, S. J. (1975) J. Sci. Food Agric. 26, 351.