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SHORT COMMUNICATION

VOLATILE FLAVOURING CONSTITUENTS OF DURIAN

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Abstract—A sample of durians from Singapore was found to owe its characteristic odour to a mixture of esters and thioethers, whereas a sample from Kuala Lumpur contained thiols rather than thioethers. Over twenty compounds were identified.

INTRODUCTION

THE DURIAN, *Durio zibethinus* Murr. (Bombacaceae), is a tree fruit which grows in a semi-cultivated manner throughout South East Asia. It is highly prized by the indigenous peoples of this region but because of its powerful odour it is repulsive to most Europeans. A full description of the fruit and proximate analyses have been given by Stanton[1] but no analysis of its volatile constituents has been published.

The odour has two distinct notes, one very strong and onion-like, the other more delicate and fruity. When the fruit is kept in a box a more foetid note also becomes evident. An analysis of the volatile flavouring constituents of this fruit is of both practical and scientific interest. Scientific interest lies in the fact that the durian is considered by some botanists to be one of the most primitive of the trees in the tropical rain forest.[2] A knowledge of the chemistry of this fruit may well contribute to the understanding of the relationship between *Durio* and other rain forest trees.

RESULTS AND DISCUSSION

The distillation of the arils under reduced pressure gave an aqueous distillate (65 ml/100 g pulp) with the characteristic odour of durian and pH 5·5–6·0. The dry residue was odourless but the addition of water produced a modified onion odour totally lacking in fruitiness.

Small portions of distillate were tested with hydrochloric acid, potassium carbonate, hydroxylamine hydrochloride, hydroxylamine in alkaline solution, mercuric chloride and *p*-dimethylaminobenzaldehyde[3] to determine their effect on the odour. Mercuric chloride removed the onion odour immediately leaving the fruity note unchanged. Acid and alkali removed the fruity odour slowly and alkaline hydroxylamine removed it immediately. It was concluded that thiols or thioethers were responsible for the onion odour and esters for the fruity odour. Carbonyls and indoles were either absent or unimportant.

Since the onion odour was removed from the Singapore durians by chloramine-*T* but not by phenylmercury acetate, this odour was attributed to thioethers, but in order to confirm this and also to identify the thioethers, the reactions were repeated on a large scale.

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[1] W. R. STANTON, *Trop. Sci.* **8,** 6 (1966).

[2] E. J. H. CORNER, *Ann. Bot.* **13,** 367 (1949).

[3] F. FEIGL, *Spot Tests in Organic Analysis* (7th Edition), p. 38, Elsevier, Amsterdam (1966).

Phenylmercaptides and sulphinimines were isolated and analysed by TLC.[4] Decomposition of the crude phenylmercaptides with dithizone gave only a faint and fugitive onion odour and no phenylmercaptides could be detected by TLC. It was clear that thiols did not make a significant contribution to the odour.

Reduction of the sulphinimines with tin and HCl gave a strong odour of onion and three distinct spots were obtained by TLC. The major component was identified tentatively as diethyl thioether, a minor component appeared to be the derivative of dimethyl thioether, and the third had an RF value rather lower than that of the dipropyl thioether derivative and was probably due to either methyl propyl thioether or ethyl propyl thioether.

When the investigation of the Singapore fruit had ceased for lack of material, durians were obtained from Kuala Lumpur. On repeating the tests with phenylmercury acetate and chloramine-T, however, it was found that the onion odour of the Kuala Lumpur fruit was due mainly to thiols. Thioethers were detected by smell when the sulphinimines were reduced with tin and HCl but were not present in sufficient quantity to be detectable by TLC. Analysis of the phenylmercaptides by TLC gave spots with R_f values equal to those of derivatives of methanethiol, ethanethiol and propanethiol; the last was by far the largest and its identification was confirmed by comparing the mass spectrum of the phenylmercaptide with that of an authentic specimen.

These results lead to the conclusion that the substances responsible for the onion odour of durians purchased in Singapore in 1969 were thioethers together with a minute amount of thiols, whereas the reverse was true of the fruit obtained from Kuala Lumpur in 1970. However tentative the identification of individual thioethers might be, the method used clearly distinguishes between thiols and thioethers.

Since both samples were bought in markets, nothing is known about the variety of tree from which they came, and the Malayan fruit was purchased about 2 months earlier than that from Singapore. Hence the chemical differences between them could reflect either botanical or seasonal variations.

Propanethiol and diethyl thioether both have onion-like odours. Hydrogen sulphide and diethyldisulphide were also identified in condensed headspace vapours by mass spectrometry as described in the Experimental section; it is possible that these compounds were responsible for the unpleasant foetid odour, suggested by some authors to be due to indoles.

An *iso*-pentane extract prepared from the Singapore fruit was examined in a gas chromatograph fitted with a 1:1 stream-splitter between the column and the detector so that the odour of the compounds could be determined simultaneously with the appearance of the peak on the recorder. The extract gave a chromatogram containing 17 peaks, one of which was much larger than the others, had a very strong fruity odour and was clearly the principal constituent of the fruity note although some of the other smaller peaks had weaker fruity odours. This experiment has been described in greater detail elsewhere.[5] Similar experiments with more concentrated extracts in 'Freon 11' (fluorotrichloromethane) prepared from the second sample of fruit revealed the presence of six more peaks, some of which had strong odours varying in character from fruity to foetid, but the large peak with the fruity odour still appeared to be the most important and was identified by GLC–MS examination of condensed headspace vapours as ethyl α-methylbutyrate. The 'Freon 11' extracts were between 200 and 400 times as concentrated as the original distillate, and it is

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[4] G. E. HOWARD and J. BALDRY, *Analyst.* **94,** 589 (1969).

[5] G. E. HOWARD, *Proc. Conference on Tropical and Subtropical Fruits (Tropical Products Institute)* p. 241 (1969).

likely therefore that most of the minor constituents were of little importance individually, although their combined effect might be important.

TABLE 1. VOLATILE FLAVOURING COMPOUNDS OF DURIAN

Hydrogen sulphide		Methyl acetate	(1)
Methanethiol	*	Ethyl acetate	(3)
Ethanethiol	*	Methyl propionate	(3)
Propanethiol		Ethyl propionate	(1)
Dimethylthioether	*	*n*-Propyl propionate	(1)
Diethylthioether	*	Ethyl *iso*-butyrate	(1)
Diethyldisulphide	(1)	Ethyl butyrate	
Methanol	(2)	Methyl α-methylbutyrate	(2)
Ethanol	(5)	Ethyl α-methylbutyrate	(5)
n-Propanol	(4)	*n*-Propyl α-methylbutyrate	(1)
3-Methylbutan-1-ol		Ethyl iso-valerate	(1)
Acetaldehyde	(1)	Ethyl methacrylate	(1)
Propionaldehyde	(2)	Ethyl benzene	(1)

The relative proportions are based on the height of the GLC peaks as a percentage of recorder full-rate deflection: (1) 10; (2) 10–30; (3) 30–60; (4) 60–100; (5) over 100%. Compounds marked * were identified by TLC in one solvent. All other compounds were identified by their MS obtained from condensed headspace vapours. Identifications were confirmed by comparing MS and chromatograms with those of authentic specimens.

In order to confirm the conclusion that propanethiol and ethyl α-methylbutyrate were the predominant constituents of the odour of durian, an aqueous solution containing 2·5 ppm of propanethiol and 20 ppm of ethyl α-methylbutyrate was prepared. The odour of the resulting mixture was very similar in character to that of durian although it was not a precise imitation. The result was considered to be very satisfactory, however, since several substances present in the fruit in concentrations approaching half that of ethyl α-methylbutyrate were omitted from the synthetic mixture.

EXPERIMENTAL

Materials. Six durians were obtained in Singapore in September 1969 and eight in Kuala Lumpur (Malaysia) in July 1970. In both cases, the partially ripened fruit was sent to London by air in large sealed cans. The durians were allowed to ripen at room temp.; those that could not be processed immediately were dissected and the flesh (arils) was frozen in solid CO_2 and stored at −20°. The average wt of a fruit was 1466 g, consisting of skin 60·3%, seeds 18·5% and edible aril 21·2%.

Distillation of fruit. The pulp (750 g) was placed in a 2-l. wide-mouthed flask and was frozen by cooling in solid CO_2. H_2O and other volatiles were distilled (pressure 2 torr) into a series of 3 cold traps, 2 of which were cooled in solid CO_2 and the last in liquid N_2. The flask was heated at 20–30° but the pulp remained frozen throughout the distillation. Distillates were stored in stoppered flasks at −20° until they were required.

Thiols—preparation and analysis of phenylmercaptides. Phenylmercury acetate was allowed to react at 2° with 200 ml of the distillate and was then distilled to dryness.[4] The distillate was used for the identification of thioethers. The remainder of the residue was purified to remove decomposition products and the excess of reagent by chromatography on a column containing 2·5 g of acid-washed silica gel packed as a slurry in light petroleum (b.p. 40–60°). The crude phenylmercaptide mixture was dissolved in Et_2O, light petroleum was added until the derivative began to precipitate and sufficient Et_2O was added to redissolve the precipitate. This solution was poured on to the column and the solute was eluted with a mixture of ether and light petroleum (b.p. 40–60°) (1:9). Fractions (0·5 ml) were collected and tested for purity by TLC. The first fraction contained only impurities, the next 9 fractions contained phenylmercaptides and subsequent fractions contained only impurities. The purified mixture of phenylmercaptides was analysed by TLC with silica gel 200 μm thick.[4] The chromatograms were developed with Et_2O–petrol (1:9).

Thioethers—preparation of sulphinimines. Chloramine-T was added to the distillate from the preparation of phenylmercaptides to convert thioethers into sulphinimines.[4] The product of the reaction was analysed by TLC on silica gel 200 μm thick.

Concentration of volatile constituents for GLC. He (150 ml at 1 ml/min) was passed through the aqueous distillate (10 ml) which had been saturated with Na_2SO_4 and the volatile substances were condensed in a gas sampling valve the trap of which consisted of Cu tubing packed with 5% 'Carbowax 20M' on 'Universal B' 80–100 mesh support and cooled in liquid N_2. When the condensation phase of the operation was complete, the Dewar flask of liquid N_2 was removed and replaced with hot water. The valve was then operated to sweep the volatilized material into the chromatograph. Solvent extracts were prepared from the aqueous distillates in standard liquid–liquid extractors and concentrated by distilling the excess of solvent through short column packed with glass helices.

Gas chromatography. Column 5·5 m × 2 mm Cu tube packed with 5% polypropylene glycol (Ucon-LB-550-X) on acid-washed DCMS treated 'Chromosorb W' 80–100 mesh. Carrier gas-He, flow-rate 25 ml/min. Temperature programme: 15 min at 55° then increased at 2°/min to 150°. Detector: flame ionization.

Identifications. Although EtOAc and methyl propionate were obscured by the large EtOH peak, these compounds were identified by scanning repeatedly during the passage of the combined peak. Thiols and thioethers were not detected by GLC. The lower members of these series do not give a good response with the flame ionization detector, and in ng quantities are often adsorbed by metallic components on GLC.

Key Word Index—Durio zibethinus; Bombacaceae; durian; volatile flavours; esters; thioethers; thiols