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Note

Separation of nitromusks by capillary gas chromatography

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Musk ambrette [1-(1,1-dimethylethyl)-2-methoxy-4-methyl-3,5-dinitrobenzene] and musk xylene [1-(1,1-dimethylethyl)-3,5-dimethyl-2,4,6-trinitrobenzene] belong to the class of benzenoid synthetic nitromusks. They are widely used in manufacturing of cosmetics and toiletries[1,2] instead of natural musks, which are much more expensive and insufficiently available to satisfy the commercial demand.

The widespread use of nitromusks is not yet free from risks to humans: some authors have pointed out the occurrence of photoallergic reactions[3–5] caused by musk ambrette; and moreover peroxides produced by the photodecomposition of nitromusks may be involved in skin cancer promotion[6].

It is therefore necessary to develop a simple and reliable method for the identification of nitromusks. Betts *et al.*[7] have suggested the use of electron-capture gas chromatography (GC), but they found some difficulties in resolving musk ambrette from musk xylene, owing to the closely similar retention times of these two compounds on both polar and non-polar stationary phases.

A sharp distinction between these two nitromusks is of a great importance for the verification of the presence of musk ambrette, which is so far the only nitromusk that has been shown to be responsible for photoallergic contact dermatitis.

In order to achieve a clear resolution of musk ambrette from musk xylene, we decided to use capillary GC.

EXPERIMENTAL

Apparatus and material

A Carlo Erba Model 4200 gas chromatograph was used, fitted with a ^{63}Ni electron-capture detector and a split-splitless injector. A fused-silica column (30 m × 0.32 mm I.D.) was employed, with OV-17 liquid phase (film thickness 0.3 μm). The chromatograph was connected to a recorder-integrator (Hewlett-Packard 3390 A).

The nitromusks were kindly donated by Esperis (Milan, Italy).

Procedure

A stock solution of each nitromusk was prepared, containing *ca.* 1000 mg/l each of musk ambrette and musk xylene in absolute ethanol. Working solutions

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were then prepared with a constant concentration of musk ambrette (100 ng/ml) and concentrations of musk xylene ranging from 1 to 100 ng/ml; analogous working solutions were prepared with the same concentration of musk xylene (100 ng/ml) and concentrations of musk ambrette ranging from 1 to 100 ng/ml. The two series of solutions were then tested according to the operating conditions listed in Table I.

RESULTS AND DISCUSSION

A sharp resolution of musk ambrette from musk xylene was always achieved, in both mode A (Fig. 1) and mode B. In mode A the interferences of extraneous peaks were minimized, and in mode B the analysis time was shorter, with a sharper resolution between the two peaks of interest. In the first case the minimum detectable

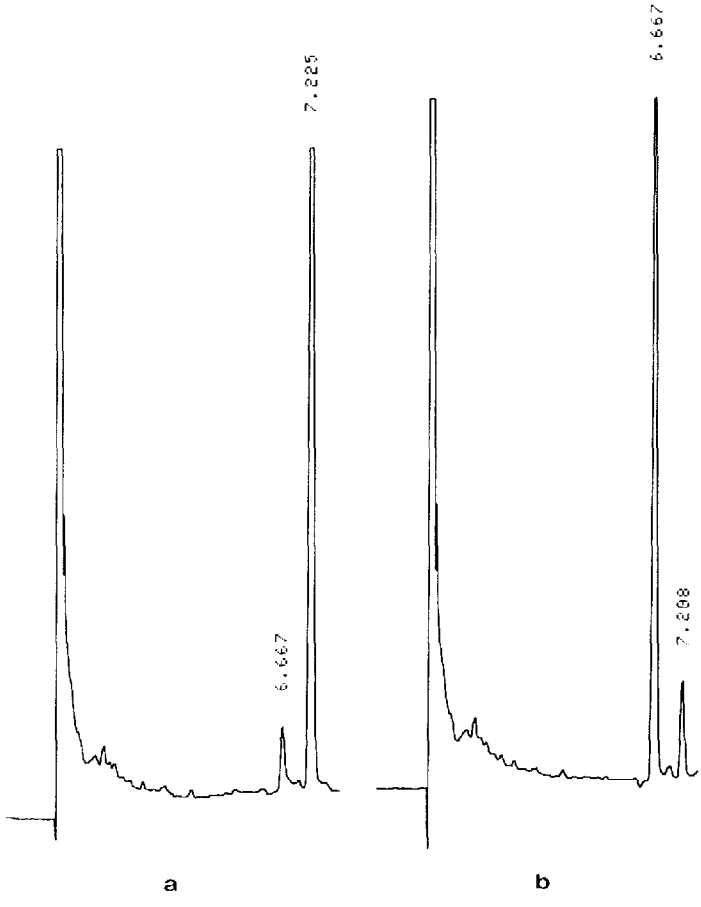

Fig. 1. Chromatograms of working solutions: (a) musk ambrette, 10 ng/ml; musk xylene, 100 ng/ml; (b) musk ambrette, 100 ng/ml; musk xylene, 10 ng/ml. Operating conditions as listed in Table I, mode A. Musk ambrette is the peak with a retention time of 6.667; musk xylene is the peak with a retention time of 7.225 (a) or 7.208 (b). In mode B (not shown in this figure) retention times were *ca.* 5.035 and 5.650 for musk ambrette and musk xylene, respectively.

TABLE I

OPERATING CONDITIONS

The detector was always operated in the constant current mode: pulse width, 1 μs; voltage, 45 V.

	Mode A	*Mode B*
Injection mode	Split	Splitless
Split ratio	1:30	–
Carrier	Nitrogen	Nitrogen
Carrier flow-rate	1.5 ml/min	2.5 ml/min
Scavenger flow-rate	20 ml/min	20 ml/min
Injector temp. (°C)	230	200
Detector temp. (°C)	250	225
Oven temp. (°C)	210	180
Injected volume	1 μl	0.5 μl

concentration was 2 ng/ml for musk ambrette and musk xylene; in the second it was 5 ng/ml for both nitromusks.

Numerous toiletries were tested in accordance with the operating conditions proposed. This confirmed that the use of open tubular columns, as used for this work, overcomes the obstacle of the separation of musk ambrette from xylene, which is not otherwise obtainable with packed columns.

The method proposed here can be helpful for the rapid and reliable detection of musk ambrette in commercial supplies that have caused photoallergy or could cause it. It could also be used to verify the purity of raw materials used by manufacturers, by detecting any adulteration of musk ambrette with musk xylene.

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