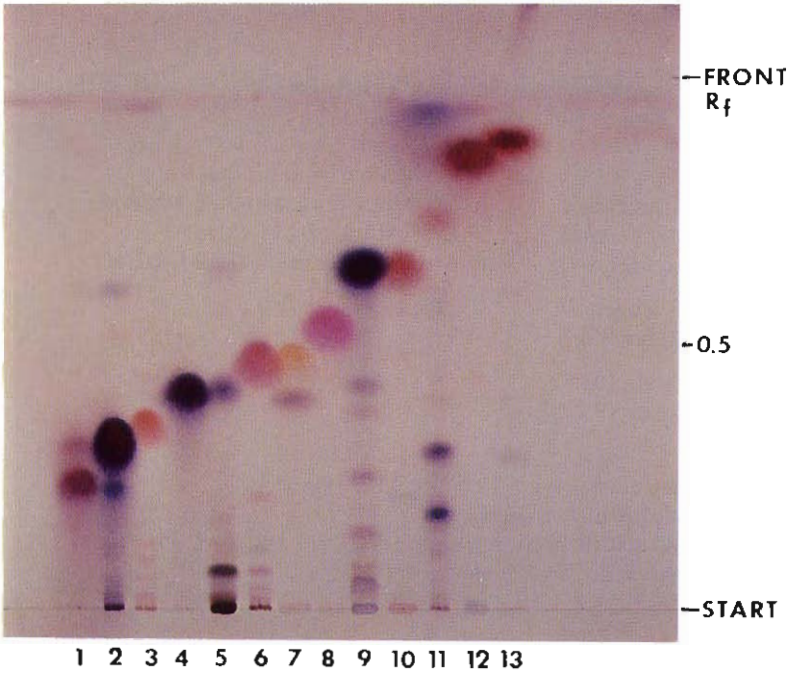
6.6 Terpene and Phenylpropane Reference Compounds

Reference compound[1]	R_f value	Colour
Fig. 1 Compounds applied in order of increasing R_f value and decreasing polarity		
1 borneol	0.24	violet-blue
2 linalool	0.30	blue
3 piperitone	0.35	orange-red
4 cineole	0.40	blue
5 citral	0.42	blue-violet
6 carvone	0.46	red-violet
7 eugenol	0.47	yellow-brown
8 thymol	0.52	red-violet
9 citronellal	0.65	blue
10 apiol	0.65	red-brown
11 myristicin	0.75	red-brown
12 anethole	0.85	red-brown
13 safrole	0.87	red-brown
Fig. 2 **Monoterpene alcohols and their esters**		
14 geraniol	0.22	blue
15 geranyl acetate	0.64	blue
16 nerol	0.24	blue
17 neryl acetate	0.66	blue
18 borneol	0.24	blue-violet
19 bornyl acetate	0.65	blue-violet
20 menthol	0.28	blue
35 menthyl acetate	0.72	blue
22 linalool	0.33	blue
23 linalyl acetate	0.68	blue
Solvent system	toluene-ethyl acetate (93:7)	
Detection	Vanillin-sulphuric acid reagent (VS No.42) →vis	

After treatment with the VS reagent the monoterpene alcohols and their esters, cineole, the aldehyde citral and citronellal show blue or blue-violet colour in vis. The phenylpropane derivatives safrole, anethole, myristicin, apiol and eugenol are brown-red/violet, while thymol and carvon are red to red-violet; piperitone shows a typical orange colour.

Commercially available reference compounds often show additional zones at the start or in the low R_f range. This can be due to resinification, decomposition products or incompletely removed impurities.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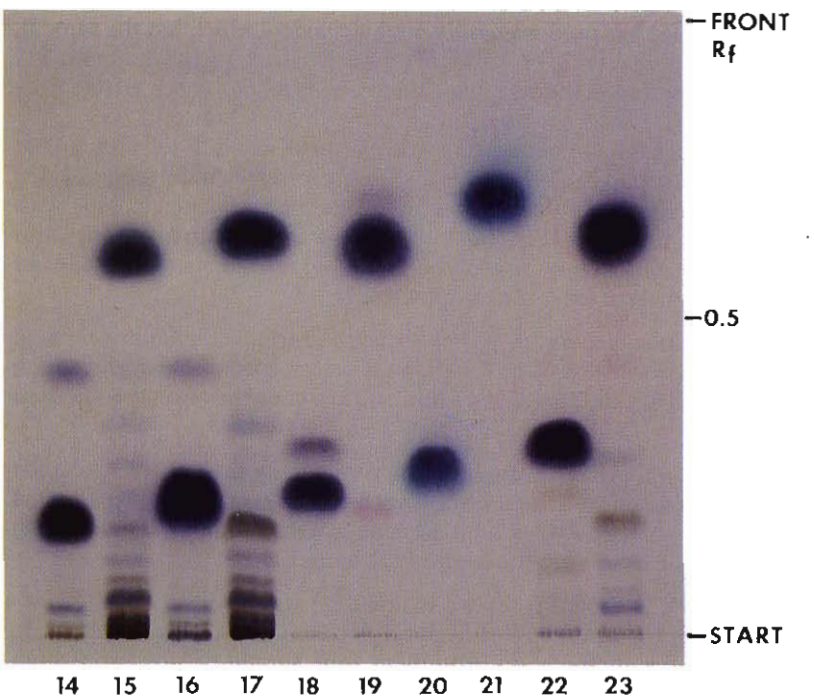
1 2 3 4 5 6 7 8 9 10 11 12 13

Fig. 1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14 15 16 17 18 19 20 21 22 23

Fig. 2

6.7 Chromatograms

Anisi fructus, Foeniculi fructus, Basicili herba, Sassafras lignum

Essential oils with anethole/methylchavicol or safrole

Drug sample (essential oil)

1 Anisi fruct. aeth. (anise)
2 Anisi stellati fruct. aeth. (staranise)
3 Foeniculi fruct. aeth. (bitter fennel)
4 Foeniculi fruct. aeth. (sweet fennel)
5 Basilici herba aeth. (basil)
6 Sassafras lignum aeth. (sassafras)
7 Anisi fruct. (DCM-extract)
8 Anisi stellati fruct. (DCM-extract)

Reference compound

T1 anethole
T2 safrole
T3 eugenol
T4 fenchone

Solvent system

Fig. 3A+B toluene-ethyl acetate (93:7)
Fig. 4A+B toluene-ethyl acetate (93:7)
Fig. 4C toluene

Detection

Fig. 3A+B Vanillin-sulphuric acid reagent (VS No. 42) →vis
Fig. 4A Concentrated sulphuric acid → vis.
B Phosphormolybic acid/K permanganate (PMS/PM No. 34 + 36) → vis
C Vanillin-sulphuric acid (No.42) → vis

Fig. 3A, B The major constituent of the essential oils 1–6 is detectable VS reagent as a red-violet to brown-violet zone at R_f 0.9–0.95. In the essential oil of anise (1), staranise (2), bitter fennel (3) or sweet fennel (4) it is anethole (T1) with small amounts of the isomer methylchavicol, while basil (5) has predominantly methylchavicol which has the same R_f value as anethole. The prominent zone of sassafras oil (6) is safrole (T2). Anethole (T1) and safrole (T2) can be separated in the solvent toluene (see Fig. 4C), where safrole then shows a higher R_f value.

The blue zones in the R_f range 0.1–0.4 of the oils 1–6 are terpene alcohols (e.g. linalool at R_f 0.4) at a very low concentration in the samples 1–2, slightly higher in bitter fennel (3) and sweet fennel (4), while basil (5) shows three intensive blue terpene alcohols with linalool as a major compound. In basil oils, linalool can be the predominant compound with very little methylchavicol (chemo- or geotype). A red-violet zone at $R_f \sim 0.5$, as in samples 2–5, can occur (e.g. epoxidihydrocaryophyllene).

Fig. 4A Anethole at $R_f \sim 0.9$ and anisaldehyde at $R_f \sim 0.45$ with concentrated sulphuric acid immediately give a red to red-violet colour. Fenchone is detected as a yellow ochre zone at $R_f \sim 0.5$ after being heated at 110°C for about 5 min and at a concentration greater than $>100\ \mu g$.

B Fenchone, if present in a lower concentration, can be detected by the PMA/PM reagent only. The dark blue-coloured zone of fenchone (T4) is seen in the sample of bitter fennel (3) (12%–22% fenchone), whereas a weak whitish zone is detected in sweet fennel (4) (0.4%–0.8% fenchone). Fenchone is absent in anise (1) or star anise.

C Detection with VS reagent (110°C/5 min) reveals in anise (7) and staranise (8) the grey-violet zones of anethole (T1) at R_f 0.8 and of triglycerides (in DCM extracts only) at R_f 0.2–0.3. In the R_f range above anethole, no prominent zone should be present. A high amount of safrole (T2) instead of anethole might indicate an adulteration with the poisonous Illicium anisatum (syn.I. religiosum).

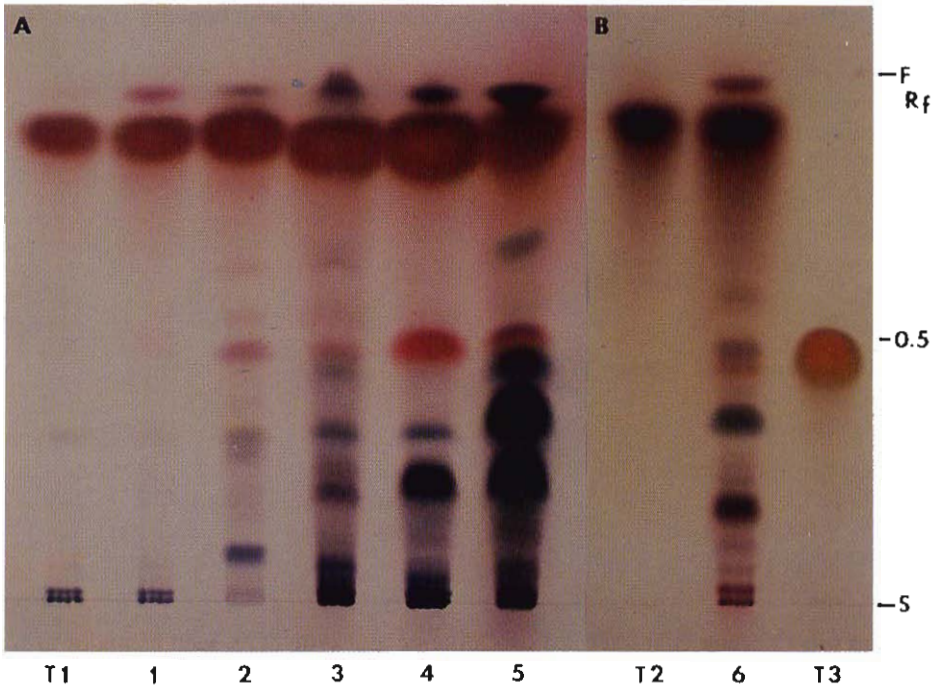

Fig. 3

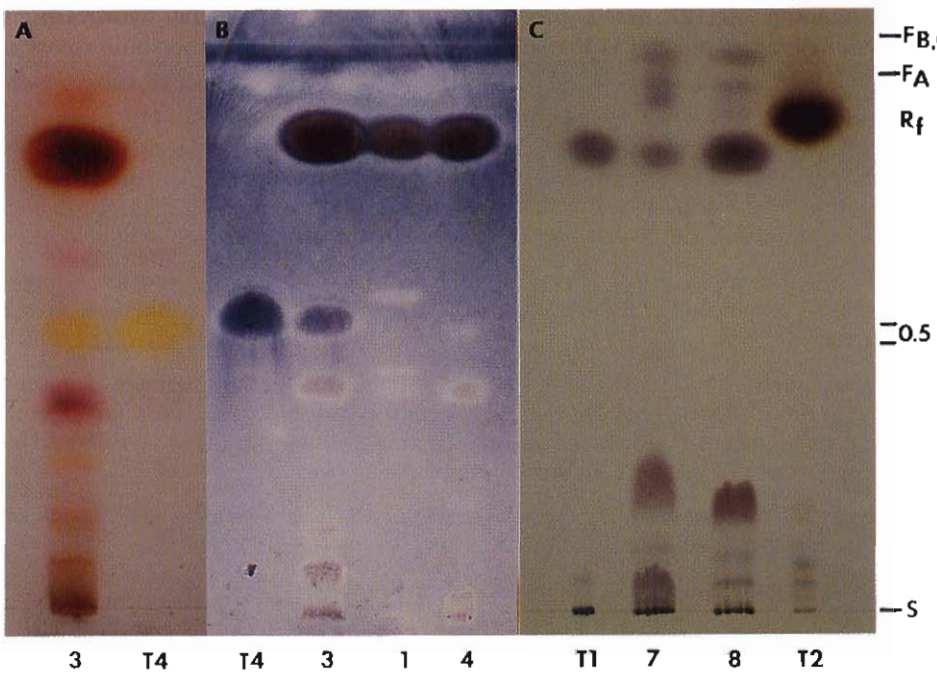

Fig. 4