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Thin-layer chromatography of some monoterpene alcohol trimethylsilyl ethers

Trimethylsilyl (TMS) ethers of alcohols have been extensively used to facilitate gas chromatographic studies since their initial applications to steroids¹ in 1962. Last year, BROOKS AND WATSON² introduced the chromatography of TMS ethers on thin layers, steroids again being the stimulus for the innovation. We have examined TMS ethers of monoterpene alcohols in an attempt to resolve some of these alcohols on thin layers without using special plates (*e.g.* containing silver nitrate³⁻⁵ which rapidly darkens) or prolonged or drastic processing (*e.g.* forming dinitrobenzoates⁶ or dehydrogenating⁷). The method has been applied to detect citronellol in the presence of geraniol in rose and related oils, and to note the appearance of monoterpene alcohols in steam-distilled or chemically oxidised limonene.

Experimental

Preparation of trimethylsilyl ethers. To a solution of monoterpene alcohol or a mixture containing such substance in 1 ml equal parts dry pyridine and *n*-hexane, 0.1 ml hexamethyldisilazane and one drop trimethylchlorosilane were added. The mixture was shaken for 1 min, then left 10 min at room temperature to settle before spotting on the thin-layer plate.

Thin-layer chromatography. Silica Gel G plates were waterspread 0.25 mm thick and dried at 105° for 30 min. Applied spots of TMS ethers were allowed to lose most of their pyridine odour before putting the plate in the solvent tank, which was lined with absorbent paper. The plate was removed when the solvent had risen 10 cm above the starting line, and sprayed with 2% vanillin in concentrated sulphuric acid, without heating. Results are given in Table I.

Limonene steam-distillation products. 4 ml limonene was co-distilled with water twenty times in succession, each condensate was extracted with a little *n*-hexane and it was returned to the still nineteen times. The final *n*-hexane extract was dried over anhydrous sodium sulphate and passed through a column of 10 g silica gel. Unchanged limonene was removed with *n*-hexane, and limonene-oxidation products subsequently eluted with pyridine. TMS ethers were formed from a portion of the pyridine eluate.

Limonene chemical oxidation products. 4 ml limonene was warmed with 10 ml 10% chromium trioxide in glacial acetic acid for 3 min, then water was added and the mixture extracted with a little *n*-hexane. The extract was washed with water till acid-free, then processed as for the final *n*-hexane extract of the steam-distillate above.

Discussion

On ordinary silica gel plates, geraniol and citronellol (dihydrogeraniol) cannot be resolved. By forming their TMS ethers they can be separated on such plates, and their presence or absence noted in rose-type oils. Thus palmarosa oil is distinct in being deficient in citronellol. The formation of TMS ethers for this purpose is relatively simple, and even if the reaction is incomplete, unchanged alcohols remain near the starting line and do not interfere. This is because solvent systems of very low polarity

TABLE I

THIN-LAYER CHROMATOGRAPHY OF MONOTERPENE ALCOHOL TRIMETHYLSILYL ETHERS

| Solute | Colour of sprayed spot | | Average R_F value with solvent system | |
|---------------------------|------------------------|---------------|--|--|
| | Initially | After 24 h | <i>n</i> -Hexane- benzene (1/1, v/v) | Petroleum spirit (60-80°)- benzene (4/1, v/v) |
| Geraniol | Dark purple | Fading green | 0.30 | 0.16 |
| Dihydrocarveol | Brown | Blue | 0.40 | 0.23 |
| Carveol | Purple | Blue | 0.41 | 0.23 |
| Citronellol | Pale brown | Deep sky blue | 0.46 | 0.33 |
| Menthol | Pale purple | Light blue | 0.52 | 0.34 |
| Linalool | Purple | Dark green | 0.64 | 0.52 |
| α -Terpineol | Grey-green | Blue | 0.64 | 0.54 |
| Fenchol | Slowly brown | Brown | 0.67 | 0.66 |
| Rose absolute | { Purple Brown | Green | 0.30 | |
| Rose otto | | Blue | 0.46 | |
| Geranium oil | | | | |
| Palmarosa oil | { Purple | Green | 0.30 | |
| Limonene steam distillate | { Purple | Blue | | 0.23 |
| Limonene chemical oxidate | { Purple | Blue | | 0.53 |
| (Original limonene) | { (Purple) | (Blue) | (0.70) | (0.60) |

are required, as the polarity of the solute alcohols has been much reduced by forming the TMS ethers.

The method does not successfully separate all monoterpene alcohols. Carveol and dihydrocarveol are not separated from each other, nor are linalool and α -terpineol. Nevertheless, it is possible to say that one or both members of each of the above pairs of alcohols is present in the limonene steam-distillation products and likewise in the chemical oxidation products. Whilst the repeated distillation used here is a laboratory manipulation, it does indicate that limonene is subject to oxidation by this treatment, yielding alcohols, and these may well appear as trace artefacts in commercial oils that contain much limonene and which are prepared by prolonged steam distillation of plant material, such as caraway. Citrus oils distilled for research purposes⁸ may also have contained such artefacts.

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