Separation of 2,4-dinitrophenylhydrazones of oxo-terpenes by thin-layer chromatography

Several chromatographic methods have been developed for the separation of terpenes as such by MILLER and co-workers[1,2]. A thin-layer chromatographic method has been developed for the identification of carbonyls in the form of their 2,4-dinitrophenylhydrazones by ONOE[3]. Paper chromatography, adsorption chromatography, counter current distribution or liquid–liquid partition are time consuming and not so handy as thin-layer chromatography (TLC). Another thin-layer chromatographic method for the separation of aliphatic carbonyls (C_1 to C_3) as 2,4-dinitrophenylhydrazones has been developed by NANO AND SANCIN[4]. The present workers have developed a new method for the separation and identification of 2,4-dinitrophenylhydrazones of oxo-terpenes by thin-layer chromatography.

Application of this procedure in conjunction with either of the afore-mentioned procedures provides valuable clues to the identity of oxo-terpenes, which are generally present in small quantities in essential oils.

Experimental

Preparation of the thin-layer plates. Thin-layer plates (20 × 5 cm) were coated with a slurry of silica gel (chromatographic, E. Merck) mixed with 10% plaster of Paris and twice its weight of distilled water. The method of application was that described by LEES AND DE MURIA[5]. The coated plates were dried at 110° for 2–3 h in an oven. Four different solvent systems were used for the separation and identification of 2,4-dinitrophenylhydrazones. No spraying agent was used as the spots themselves were distinctly coloured.

TABLE I

Synthetic mixture	*Components (as 2,4-dinitrophenylhydrazones)*
A	Carvone, menthone and pulegone
B	Menthone and pulegone
C	Salicylaldehyde, formaldehyde and phenylacetaldehyde
D	Salicylaldehyde, phenylacetaldehyde and pulegone
E	Carvone, dihydrocarvone and formaldehyde
F	Citral, α-thujone and citronellal
G	C_{10}-aldehyde, C_8-aldehyde and camphor
H	Menthone, citral and carvone
I	Acetaldehyde, camphor and acetone
J	Camphor and citronellal

Preparation of 2,4-dinitrophenylhydrazones. The method followed for the preparation of the 2,4-dinitrophenylhydrazones was as described by Guenther[6]. The derivatives were crystallized and recrystallized till they showed sharp melting points. Mixed melting points were taken to verify the authenticity of these compounds.

Solvent systems. The following solvent systems have been found to give clear separation of the synthetic mixtures of 2,4-dinitrophenylhydrazones:

S_1 = chloroform–carbon tetrachloride (1:19)
S_2 = chloroform–carbon tetrachloride (1:9)
S_3 = chloroform–carbon tetrachloride (3:17)
S_4 = petroleum ether–benzene (3:7).

The synthetic mixtures used were prepared by mixing 10 mg of each 2,4-dinitrophenylhydrazone, as shown in Table I.

A very clear separation of 2,4-dinitrophenylhydrazones in the case of the above synthetic mixtures was achieved. The results are tabulated in Table II.

TABLE II

$R_F \times 100$ VALUES OF SOME 2,4-DINITROPHENYLHYDRAZONES OF OXO-TERPENES IN VARIOUS SOLVENT SYSTEMS

S. No.	*2,4-Dinitrophenylhydrazone of*	S_1	S_2	S_3	S_4
1	Formaldehyde	9	12	13	47
2	Acetaldehyde	10	11	15	51
3	Acetone	11	13	16	60
4	C_8-aldehyde	14	19	26	69
5	C_{10}-aldehyde	16	22	30	71
6	Citral	17	20	24	63
7	Citronellal	23	37	29	30
8	α-Thujone	17	31	23	82
9	Menthone	42	38	41	84
10	Pulegone	34	37	46	75
11	Carvone	29	32	36	79
12	Dihydrocarvone	22	29	33	80
13	Camphor	25	35	39	76
14	Salicylaldehyde	5	7	8	44
15	Phenylacetaldehyde	11	16	17	58

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