CHROM. 3324

Gas chromatographic separation of 5-nitro-2-hydroxybenzal derivatives of unsymmetric hydrazines

5-Nitro-2-hydroxybenzal derivatives of unsymmetric hydrazines have been prepared and used for the separation and identification of hydrazines as well as N-nitroso compounds, the latter *via* reduction to hydrazines and formation of 5-nitro-2-hydroxybenzal derivatives. The method has been successful in the isolation of trace amounts of these compounds in complex mixtures, on a micro scale[1–5]. The separation shown in this paper was performed with derivatives of unsymmetric dialkyl-, aralkyl-, diaryl-, and cyclic hydrazines up to C_{12} as well as amino derivatives of tobacco alkaloids.

Experimental

Apparatus. For chromatography, a 2-m stainless steel tube (4-mm I.D.) packed with 2.5% w/w silicone grease (E. Merck AG., Darmstadt, Germany) on 60 to 80 mesh Chromosorb G, acid washed and DMCS treated, was used in fractometer type F6 (Perkin Elmer Bodenseewerk, Überlingen, Germany). The fractometer was equipped with a flame-ionization detector and a 2.5-mV recorder (Siemens-Kompensograph L 288 × 288) with a paper feed of 0.5 cm/min.

Procedure. The 5-nitro-2-hydroxybenzal derivatives were prepared as described earlier[2] and showed the melting points listed there.

Results

Fig. 1 shows the gas chromatographic separation of a mixture of 12 different 5-nitro-2-hydroxybenzal derivatives. Table I lists the retention times of all the derivatives tested on the 2-m column under conditions indicated in the legend of

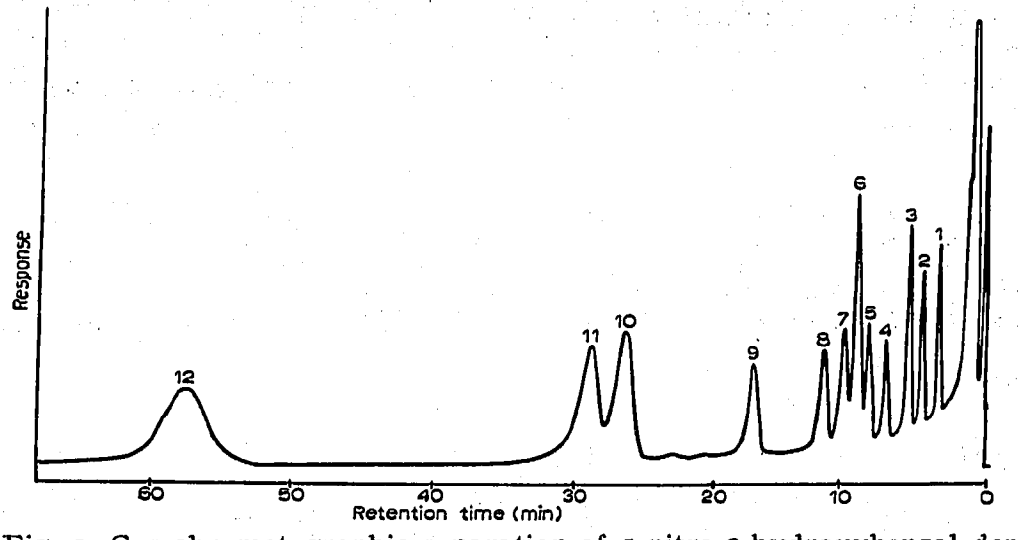

Fig. 1. Gas chromatographic separation of 5-nitro-2-hydroxybenzal derivatives of unsymmetric hydrazines. Sample size: 1 to 5 μg of each derivative in 5 μl acetic ester. Constant column temperature: 220°; injection temperature: 300°; carrier gas: helium; flow rate: 30 ml/min. 1 = 1,1-Dimethyl-hydrazine; 2 = 1-methyl-1-ethyl-hydrazine; 3 = 1,1-diethyl-hydrazine; 4 = 1-methyl-1-isobutyl-hydrazine; 5 = 1-methyl-1-butyl-hydrazine; 6 = 1,1-dipropyl-hydrazine; 7 = 1-methyl-1-pentyl-hydrazine; 8 = 1,1-diisobutyl-hydrazine; 9 = 1,1-dibutyl-hydrazine; 10 = 1-Ethyl-1-heptyl-hydrazine; 11 = 1-methyl-1-benzyl-hydrazine; 12 = 1,1-diphenyl-hydrazine.

TABLE I

RETENTION TIMES OF 5-NITRO-2-HYDROXYBENZAL DERIVATIVES OF UNSYMMETRIC HYDRAZINES

Parent hydrazine	*Retention time (min)*
1,1-Dimethyl-hydrazine	3.8
1-Methyl-1-ethyl-hydrazine	4.9
1,1-Diethyl-hydrazine	5.9
1-Methyl-1-butyl-hydrazine	8.5
1-Methyl-1-isobutyl-hydrazine	7.5
1,1-Dipropyl-hydrazine	9.3
1,1-Diisopropyl-hydrazine	8.5
1-Methyl-1-pentyl-hydrazine	10.2
1-Methyl-1-isopentyl-hydrazine	10.2
1-Ethyl-1-*sec.*-butyl-hydrazine	8.9
1-Ethyl-1-*tert.*-butyl-hydrazine	8.2
1,1-Dibutyl-hydrazine	16.0
1,1-Diisobutyl-hydrazine	11.5
1-Ethyl-1-heptyl-hydrazine	23.8
1,1-Dihexyl-hydrazine	51.8
1-Methyl-1-allyl-hydrazine	6.0
1-Ethyl-1-phenyl-hydrazine	23.4
1,1-Diphenyl-hydrazine	50.8
1-Methyl-1-benzyl-hydrazine	26.1
1-Amino-pyrrolidine	10.6
1-Amino-piperidine	12.0
1-Amino-2-methyl-pyrrolidine	11.1
1-Amino-2,5-dimethyl-pyrrolidine	11.0
1-Amino-4-methyl-piperazine	15.0
4-Amino-morpholine	11.5

Fig. 1. The retention time of the reagent 5-nitro-2-hydroxy-benzaldehyde is about 1 min, thus excluding any interference with the derivatives. The logarithm of the relative retention values was a linear function of the number of C-atoms.

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Received November 10th, 1967