Separation of positional and geometrical isomers of monoenoic aldehydes via the dinitrophenylhydrazones

Silica gel impregnated with silver nitrate used as an adsorbent for chromatography[1] possesses highly selective properties for separating substances with differences in number, position and geometrical configuration of the double bonds. This was demonstrated by application of this adsorbent in column[2,3] and especially in thin-layer chromatography[4,5].

DE JONG *et al.*[6] (*cf.* HAVERKAMP BEGEMANN AND KOSTER[7]) and URBACH[8] studied the separation of dinitrophenylhydrazones (DNPHs) of aldehydes using thin-layer chromatography on aluminium oxide impregnated with silver nitrate; BADINGS AND WASSINK[9] used silver nitrate on Kieselguhr for the same purpose. These authors described the separation of DNPHs of saturated, 2-monoenoic and 2,4-dienoic aldehydes. Moreover they separated the DNPHs of monoenoic aldehydes containing isolated *trans*- or *cis*- double bonds from DNPHs of 2-monoenoic aldehydes.

DE VRIES AND JURRIENS[5] demonstrated that the position of the double bond also exercises a certain influence on the R_F values by separating methyl esters of *cis*-6-, *cis*-9- and *cis*-12-octadecenoic acids. It could therefore be expected that DNPHs of the positional and geometrical isomers of straight-chain monoenoic C_6- and C_7-aldehydes can also be separated using silica gel G impregnated with silver nitrate.

Methods and results

The plates (20 × 40 cm), with an adsorbent layer of 0.5 mm thickness, were prepared as described by DE VRIES AND JURRIENS[5,10].

Two micrograms of each DNPH of the isomeric hexenal and heptenal series were dissolved in 10 μl carbon tetrachloride. These solutions were placed on the plate by means of a micropipet of 10 μl at a distance of 5 cm from and parallel to a short edge. In the same way the mixture of all DNPHs of the hexenal respectively heptenal series (containing 2 μg of each DNPH) was placed on the same plate.

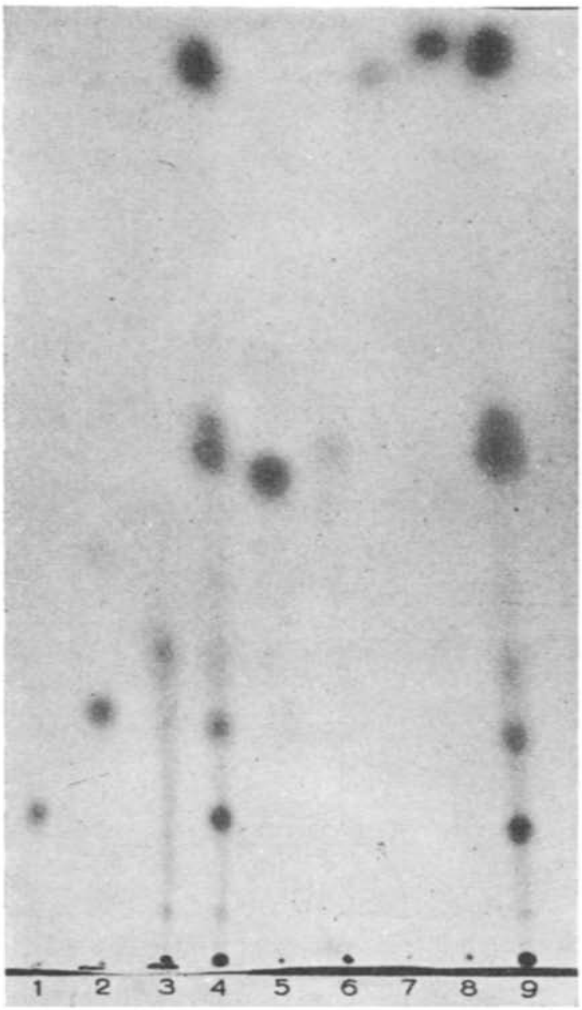
Development took place as customary using the ascending technique with benzene as eluant. During and shortly after development the DNPHs were visible as yellow spots. After storing in air all the unsaturated DNPHs turned grey. This may be helpful in distinguishing the saturated from the 2-monoenoic components, which have about the same R_F values. As can be seen from Fig. 1 for the hexenals and from Fig. 2, showing the heptenals, all the geometrical and positional isomers of both these series were clearly separated.

The *cis*-3-enals show some tailing, probably because these compounds degrade during development owing to the presence of a reactive α-methylene group in the molecule.

Discussion

The results clearly indicate that silica gel G impregnated with silver nitrate possesses highly selective adsorption properties for the separation of positional and geometrical isomers of alkenal DNPHs.

cis-4- and *cis*-5-heptenal DNPHs and *trans*-3- and *trans*-4-hexenal DNPHs have long elution times. It is therefore necessary to use longer plates.



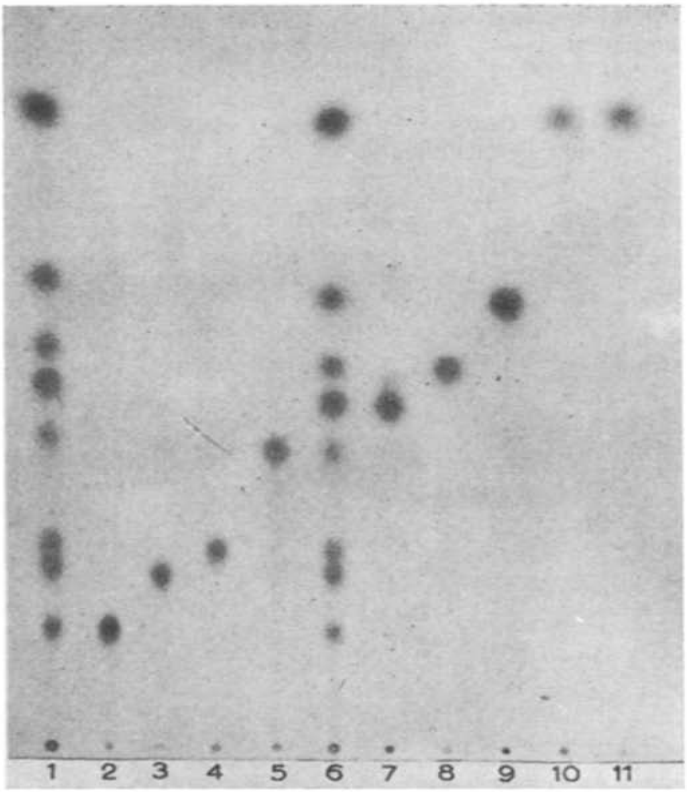


Fig. 1. Separation of a mixture of DNPHs of isomeric hexenals by TLC. Adsorbent: 30% silver nitrate–silica gel G; solvent: 100% benzene. 1 = 5-hexenal; 2 = *cis*-4-hexenal; 3 = *cis*-3-hexenal; 4 = mixture of hexanal and all isomeric hexenals; 5 = *trans*-4-hexenal; 6 = *trans*-3-hexenal; 7 = *trans*-2-hexenal; 8 = hexanal; 9 = mixture of hexanal and all hexenals.

Fig. 2. Separation of a mixture of DNPHs of isomeric heptenals by TLC. Adsorbent: 30% silver nitrate–silica gel G; solvent: 100% benzene. 1 = mixture of heptanal and all isomeric heptenals; 2 = 6-heptenal; 3 = *cis*-5-heptenal; 4 = *cis*-4-heptenal; 5 = *cis*-3-heptenal; 6 = mixture of heptanal and all isomeric heptenals; 7 = *trans*-5-heptenal; 8 = *trans*-4-heptenal; 9 = *trans*-3-heptenal; 10 = *trans*-2-heptenal; 11 = heptanal.

Only the *trans*-5- and *trans*-6-DNPHs of the nonenals were available. These nonenals could be separated using the same technique.

The technique described above may be used in the identification of unknown monoenoic aldehydes, which occur in minute amounts in oils and fats and which play an important role in imparting flavours[11] to these products. Identification and/or determination of these and other aldehydes has always been difficult in view of the extremely small amounts involved. As far as is known, attempts to separate the isomers described, by means of gas–liquid chromatography, which in itself is most suitable for analysing trace amounts, have been unsuccessful.

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Thin-layer chromatography of long-chain tertiary amines and related compounds*

Long-chain tertiary amines, *e.g.* trilaurylamine, tri-*n*-octylamine etc. are currently being examined as extraction agents in reprocessing systems for nuclear fuels. Certain commercially available amines sold as "tricaprylamine" are mixtures of straight-chain (normal) saturated tertiary amines where the alkyl groups comprise a C_8–C_{10} mixture with the C_8 chain predominating. Gas chromatographic analysis has established[1] that the main tertiary amines present are members of a homologous series: tridecyl-, didecyloctyl-, dioctyldecyl-, trioctyl-, and dioctylhexyl-amines. Secondary and primary amines with these alkyl groups are present as impurities, usually not amounting to more than 5 % by weight of the mixture. Many commercial samples of the higher *n*-alkyl tertiary amines containing only one alkyl group, *e.g.* tri-*n*-octylamine or tri-*n*-dodecylamine contain similar quantities of the corresponding secondary and primary amine impurities.

The extraction of uranium and plutonium by these long-chain amines varies according to the nature of the amino nitrogen present so that it is necessary in partition studies to be able to determine the relative amounts of primary, secondary and tertiary amine groups present in a particular sample of amine. Furthermore, if the amine has been exposed during use to conditions causing chemical degradation, *e.g.*, radiation in the presence of mineral acids, the type and amount of such degradation must be determined to define the limits of effective performance.

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