CHROM. 16,311

Note

Gas chromatographic identification of long-chain aliphatic alcohols and acetates with different degrees of unsaturation by means of three- and four-phase diagrams

V. G. BEREZKIN*

A. V. Topchiev Institute of Petrochemical Synthesis, U.S.S.R. Academy of Sciences, 29 Leninsky Prospect, Moscow 117912 (U.S.S.R.)

and

V. N. RETUNSKY

All Union Institute of Biological Control, Poltavskoje shosse 7, Kishinev 277031 (U.S.S.R.)

(Received September 23rd, 1983)

Recent interest in the chemistry of long-chain aliphatic alcohols and acetate is to a great extent due to the findings that these compounds serve as pheromones for many insects and can be successfully used in agricultural practice to achieve more effective and selective control of pests[1].

Usually, a combination of sophisticated spectroscopic (infrared and nuclear magnetic resonance with Fourier transforms) and reaction chromatography methods is utilized for the identification of these compounds[2,3]. In many cases a great deal of structural information can be derived from a careful study of the chromatographic behaviour of analyzed compounds and comparison of their parameters (relative retention times and/or Kováts indices) with tabulated data[4,5]. However, this method requires a large catalogue of predetermined parameters and its reliability and resolving power are not always high enough.

We describe here a simple technique effective for the identification of eight classes of organic compounds of similar chemical structures: saturated, monoenic and dienic (conjugated and non-conjugated) alcohols and the corresponding acetates. The identification is based on the use of a set of Kováts indices for the analyzed compounds on four stationary phases by construction of three- and four-phase diagrams similar to those used earlier for the selection of sorbents for the analysis of mixtures of compounds with different functional groups[6]. This technique is not limited to our application only and can be used in any area where only microgram amounts of the compounds of interest are available for the identification.

EXPERIMENTAL

The saturated alcohols and acetates were obtained from commercial sources. The monoenic and dienic compounds with C_{12}–C_{16} carbon skeletons were prepared by Dr. E. R. Möttus and co-workers (Tartu State University) and by Dr. B. G. Kovalev and co-workers at the Institute of Biological Control (Kishinev).

A Tswet Model 5 gas chromatograph equipped with a flame ionization detector and standard 1 m × 3 mm I.D. glass columns was used to determine retention data. All stationary phases [OV-1, OV-17, OV-225 and diethylene glycol succinate (DEGS)] were 10% coatings on 80–100 mesh Chromaton N-AW-DMCS (Chemapol, Prague, Czechoslovakia). The carrier gas was nitrogen at 30 ml/min. All chromatographic parameters were determined in the isothermal mode at 130°C. The calculation of the gas hold-up time was done according to the method described by Peterson and Hirsch[7].

RESULTS AND DISCUSSION

The presentation of the retention data in the form of Kováts indices, I, permits the identification of the components of analyzed mixtures in two ways: by searching tables or using ΔI parameters (the difference in Kováts indices of a compound chromatographed on two different stationary phases)[8]. The second approach appears to be more reliable since ΔI parameters are more reproducible and less dependent on temperature and other experimental conditions.

In general, the function, Y, characterizing the chromatographic behaviour of a certain chemical class of organic compounds on several stationary phases can be defined as

$$Y = F(\Delta I_{12}, \Delta I_{13}, \ldots \Delta I_{ij}, \ldots \Delta I_{n-1,n}) \qquad (1)$$

where ΔI_{ij} = the difference between the Kováts indices of a sorbate on two stationary phases i and j and n = number of stationary phases used. If we plot these functions for different classes of compounds in multidimensional space, we obtain certain characteristic regions wherein all the points corresponding to compounds of the same class will be located.

For practical applications of this method it is important to determine the optimal number of stationary phases required for the reliable identification of representatives of certain chemical classes of organic compounds. As an example, we investigated the ability of this technique for the identification of compounds belonging to the following eight chemical classes: saturated, monoenic and dienic (conjugated and non-conjugated) alcohols and the corresponding acetates.

For $n = 2$ (only two stationary phases are used, for example, OV-1 and OV-225), the resolving power of this method was rather poor because superimposition of ΔI values for different classes of compounds was observed (see Table I). For $n = 3$ or 4 the situation was greatly improved. Taking different cross-sections of the function (1) in multidimensional space, we obtained a set of diagrams corresponding functions of the type

$$\Delta I_{ij} = F(\Delta I_{kl}) \qquad (2)$$

where ΔI_{ij} and ΔI_{kl} = the difference in Kováts indices of the analyzed compound on stationary phases i, j and k, l respectively. The variation of the sets of ΔI_{ij} parameters permits one to obtain diagrams where the characteristic chromatographic regions of certain chemical classes are completely separated. Typical examples are shown in

TABLE I

$\Delta I_{1,3}$ PARAMETERS FOR DIFFERENT CLASSES OF ALIPHATIC ALCOHOLS AND ACETATES (C_{12}–C_{16}) ON STATIONARY PHASES OV-1 (1) AND OV-225 (3)

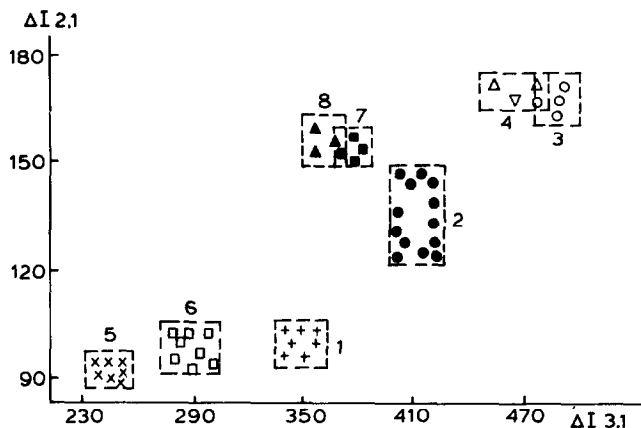| Class of compounds	$\Delta I_{1,3}$
1 Saturated alcohols	330–360
2 Monoenic alcohols	380–420
3 Non-conjugated dienic alcohols	440–470
4 Conjugated dienic alcohols	430–460
5 Acetates of saturated alcohols	240–260
6 Acetates of monoenic alcohols	280–320
7 Acetates of non-conjugated dienic alcohols	360–380
8 Acetates of conjugated dienic alcohols	350–370

Fig. 1. Two-dimensional three-phase diagram of aliphatic alcohols and acetates with different degrees of unsaturation. $\Delta I_{2,1}$ = Kováts indices difference on OV-1 and OV-17; $\Delta I_{3,1}$ = Kováts indices difference on OV-1 and OV-225. The designation of the chromatographic regions corresponds to the class numbering in Table I.
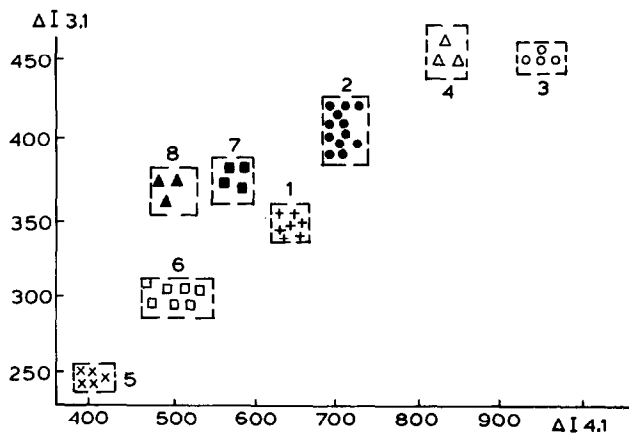

Fig. 2. Two-dimensional three-phase diagram of aliphatic alcohols and acetates with different degrees of unsaturation. $\Delta I_{3,1}$ = Kováts indices difference on OV-1 and OV-225; $\Delta I_{4,1}$ = Kováts indices difference on OV-1 and DEGS. Designation of chromatographic regions as in Fig. 1.
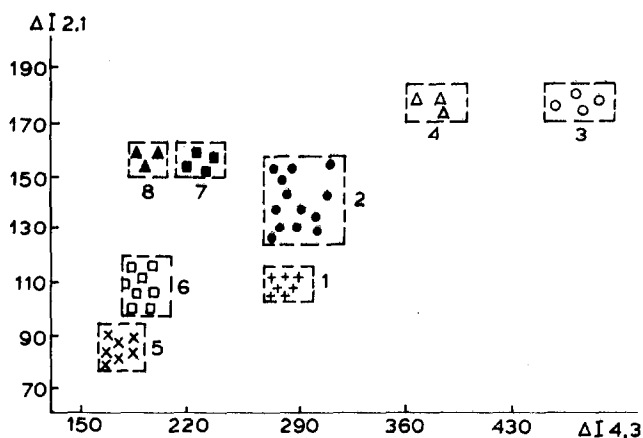
Fig. 3. Two-dimensional four-phase diagram for aliphatic alcohols and acetates with different degrees of unsaturation. $\Delta I_{2,1}$ = Kováts indices difference on OV-1 and OV-17; $\Delta I_{4,3}$ = Kováts indices difference on OV-225 and DEGS. Designation of chromatographic regions as in Fig. 1.

Figs. 1–3. In Fig. 1, all chromatographic regions but for the pairs 3 and 4 and 7 and 8 are well separated. The variation of cross-sections (Figs. 2 and 3) enabled good separation of the desired chromatographic regions (3, 4 and 7, 8).

Thus, the proposed method permits a group identification of organic compounds or the conclusion that an analyzed sorbate does not belong to the given set of chemical classes.

ACKNOWLEDGEMENTS

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