GAS-LIQUID CHROMATOGRAPHY OF TRITERPENOIDS AND THEIR TRIMETHYLSILYL DERIVATIVES

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We have previously reported the results of a study of the chromatographic mobility of triterpenoids and their derivatives on the phase SE-30 [1]. In the present paper we give the GLC results of a number of of triterpenoids on the phases SE-30 and QF-1 and of the chromatography under the same conditions of the trimethylsilyl derivatives (TMS) of triterpene alcohols. Cholestane was used as standard to calculate the relative retention volumes (Table 1).

As already mentioned [1], in the GLC of the triterpenoids the relative retention volumes rise in the sequence alcohol–ketone–acetate on the phase SE-30. The same relationship is retained for the phase QF-1, but the retention times of the compounds are considerably greater. The retention times of the substances are also affected by the number substituents – those of diols being greater than those of triterpenoids with one hydroxy group.

It is known [2] that in GLC on the phase SE-30 trimethylsilyl derivatives of polyhydroxytriterpenoids have considerably smaller retention times than the alcohols.

We used the method of Ikekawa et al. [2] to prepare the TMS ethers of the triterpenoids.

The relative retention volumes of the TMS derivative of the diols for both phases were less than the corresponding values for the initial diols. The retention times of the TMS derivatives of alcohols with one hydroxy group, on the other hand, were greater than those of the alcohols.

TABLE 1. Relative Retention Volumes of Triterpenoids and Their Trimethylsilyl Derivatives*

Triterpenoids	1,5% SE-30	3% QF-1	1,5% SE-30 TMS derivatives	3% QF-1 TMS derivatives
Taraxerol	2,90	5,34	3,24	3,57
Taraxerone	2,78	7,75	—	—
Simiarol	4,16	—	4,16	4,43
Simiarone	4,07	11,18	—	—
Friedelinol	4,45	—	5,28	6,04
Epifriedelinol	4,39	7 20	4,63	5,22
Friedelin	4,31	13,50	—	—
$\Delta^{5(10)}$-Alnusenol	—	—	—	8,17
Alnusenone	3,40	9,25	—	—
$\Delta^{5(10)}$-Alnusenol acetate	4,09	—	—	—
Campanullin	2,55	3,79	—	—
α-Amyrin	3,31	—	3,66	3,93
α-Amyrin acetate	4,83	—	—	3,52
β-Amyrin	3,03	—	3,44	—
β-Amyrin acetate	4,07	—	3,81	3,90
Lupeol	3,33	—	6,22	5,69
Betulin	7 13	—	5,72	5,19
Uvaol	6,45	—	5,10	4,90
Myricadiol	5,72	—	—	—

*Carrier gas Ar, 75 ml/min

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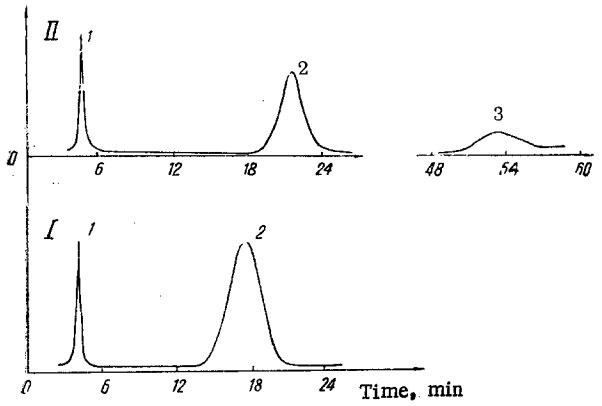

Fig. 1. Gas-liquid chromatograms: I) mixture of simiarenol and simiarenone on phase SE-30. 1) Cholestane; 2) simiarenol–simiarenone. II) Mixture of the TMS ether of simiarenol and simiarenone on phase QF-1. 1) Cholestane; 2) TMS ether of simiarenol; 3) simiarenone.

On comparing the results of the GLC of the TMS derivatives of the triterpenes on the phases SE-30 and QF-1, it can be seen that the TMS derivatives of the diols possess a greater chromatographic mobility on QF-1 than on SE-30. The retention times of the TMS derivatives of alcohols with one hydroxy group on SE-30, on the other hand, are lower than on QF-1.

We have observed previously that in chromatography on SE-30 a mixture of alcohols and the ketones corresponding to them were not separated. The use of SE-30 in the GLC of a mixture of TMS derivatives of triterpene alcohols and the corresponding ketones likewise did not lead to their separation; on the chromatogram the TMS ether of simiarenol and simiarenone gave a single peak (4.18), just as for the TMS ether of epifriedelinol and friedelin (4.35).

The use of QF-1 in the chromatography of these and similar mixtures enabled them to be separated completely (Fig. 1). The α- and β-amyrins were separated on SE-30, and the TMS derivatives of these compounds were separated on QF-1, which agrees with information in the literature [2].

In plants, triterpenoids are frequently accompanied by steroids, especially β-sitosterol, and therefore we chromatographed a mixture of α- and β-amyrins and β-sitosterol. The relative retention volumes of these substances are fairly close (for β-sitosterol on SE-30 3.06, and for the TMS ether of β-sitosterol on QF-1 3.05).

We were unable to separate these substances and their TMS derivatives on either SE-30 or QF-1.

EXPERIMENTAL

The gas-liquid chromatography was performed on a "Pye" instrument, series 104, with a flame ionization detector (consumption of Ar, 75 ml/min). Glass columns (100 × 0.4 cm) containing 1.5% of SE-30 on Gas-Chrom G (60-80 mesh) at a column temperature of 240° C and glass columns (150 × 0.4 cm) with 3% of QF-1 on Gas-Chrom Q (85-100 mesh) at a column temperature of 220° C were used. Samples of pure reference materials – 1 μl of a 0.5% solution in chloroform – were introduced into the column by means of a Hamilton syringe.

Preparation of the Trimethylsilyl Derivatives. A solution of 2 mg of the substance concerned in 0.2 ml of dry pyridine was treated with 0.1 ml of hexamethyldisilazane and 0.1 ml of chlorotrimethylsilane. After the reaction mixture had been shaken vigorously for 3 min, it was left for 5 min at room temperature and then 1-3 μl of the mixture was introduced directly into the chromatograph.

SUMMARY

1. The chromatographic mobility of TMS derivatives of triterpenoids on the phases SE-30 and QF-1 has been studied.

2. It has been shown that the best results are obtained by a combination of the phases SE-30 and QF-1 in the GLC of mixtures of triterpenoids and their TMS derivatives.

LITERATURE CITED

1. G. A. Fokina and N. V. Belova, Khim. Prirodn. Soedin., 7, 30 (1971).
2. N. Ikekawa, S. Natori, H. Itokawa, S. Tobinga, and M. Matsui, Chem. Pharm. Bull., 13, (3) 316-319 (1965).