RESOLUTION OF *n*-ACIDS AND *n*-ALCOHOLS BY "ADSORPTION" CHROMATOGRAPHY ON KIESELGUR FILMS

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INTRODUCTION

It is generally believed that the resolution of mixtures of aliphatic compounds belonging to a homologous series is not possible by normal adsorption chromatography if the compounds contain more than about ten carbon atoms each. Resolution of mixtures of this type, *e.g.*, *n*-alcohols or *n*-acids is usually performed by reversed-phase partition chromatography[1]. If adsorption chromatography could be adapted to give a degree of resolution comparable with that obtainable by reversed-phase partition chromatography, the former would be preferable because it is more rapid and much simpler.

Adsorption chromatography is normally carried out on silicagel or alumina, and experience has shown that alcohols and acids can be chromatographed only by using relatively polar solvents. Under these circumstances, the difference between the eluting effect of the solvent and the restraining effect of the adsorbent is the same for all higher members of a homologous series, so that the mixture cannot be resolved into its components.

There are, nevertheless, small differences in the polar/non-polar balance between members of a homologous series. We have explored the possibility of magnifying the effect of these minor differences by simultaneously decreasing both the restraining power of the adsorbent and the eluting power of the solvent. The results showed that the hitherto unexpected resolution of homologous, even-numbered alcohols and acids containing more than ten carbon atoms, was possible by "adsorption" chromatography on kieselgur G, using cyclohexane as the developing solvent.

EXPERIMENTAL

Kieselgur G and water (30 g/60 ml) were thoroughly mixed and spread over six glass plates (15 × 20 cm) using a device similar to that described by STAHL[2]. After the films had been allowed to dry on the bench for 3 h they were ready for use. Samples of the *n*-alcohols and the *n*-acids were made into 0.5 % and 0.25 % solutions (respectively) in ether, and 1 μl aliquots were used for chromatography; the mixtures contained 1 μg of each component. Development of the chromatograms with cyclohexane, in tanks lined with filterpaper soaked in the solvent, for a distance of 10 cm, required about 35 min. To render the alcohols visible, the solvent-free film was sprayed

with concentrated sulphuric acid and the chromatoplate was heated to 160° for 10 min. The chromogenic reagent for the acids was 0.5 % bromocresol green in ethanol, adjusted to pH 6.

RESULTS AND DISCUSSION

Fig. 1 shows that it is possible to resolve and to identify a mixture of all the even-numbered, aliphatic alcohols from *n*-decanol to *n*-tetracosanol. In addition, *n*-octanol and *n*-hexacosanol may also be distinguished, but with a lower degree of certainty.

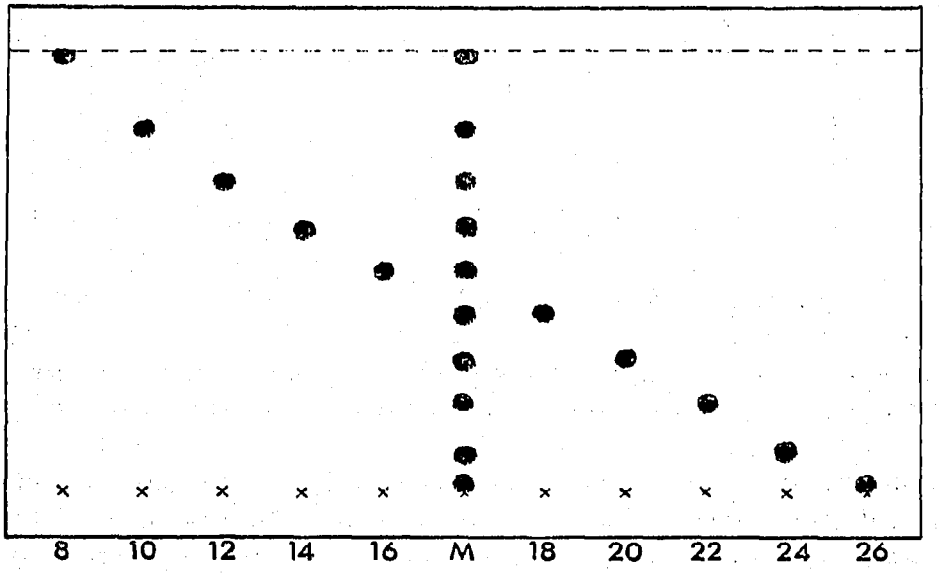

Fig. 1. Resolution of the *n*-alcohols by "adsorption" chromatography. The numerals indicate the number of carbon atoms in each alcohol. M is a mixture of all the test samples. (Substrate: kieselgur G. Solvent: cyclohexane. Chromogenic reagent: sulphuric acid).

Fig. 2 shows that the identification of the even-numbered acids containing between eight and fourteen carbon atoms presents no difficulty. Acids containing between sixteen and twenty-two carbon atoms per molecule are less well separated from one another. Although the R_F values are appreciably different, the resolution is not sufficient for an unequivocal identification if the length of the chromatogram is only 10 cm. Development of the chromatogram for a longer distance will result in a better resolution and a correspondingly higher degree of certainty in the identification.

The tailing effect which is observed only with the acids, is very dependent on the load. If the load is progressively increased beyond 2.5 μg per acid, tailing rapidly becomes bad enough to spoil the chromatogram. If a small amount of acetic acid (0.5 %) is added to the developing solvent to prevent tailing, the mobilities of all the acids are greatly increased and the differences between their R_F values are substantially diminished.

Not only do the acids exhibit an undesirable tendency to tail but the range of molecular chain-lengths which can be resolved is rather restricted. Nevertheless, a useful degree of resolution is obtainable by chromatography on kieselgur G, particularly if the chromatogram is developed for a distance exceeding 10 cm. Resolution of the alcohols is sufficiently good to be comparable with that obtainable by the slightly more discriminating but much more time-consuming process of reversed-phase partition chromatography.

It was observed that the R_F values of the alcohols and the acids varied slightly

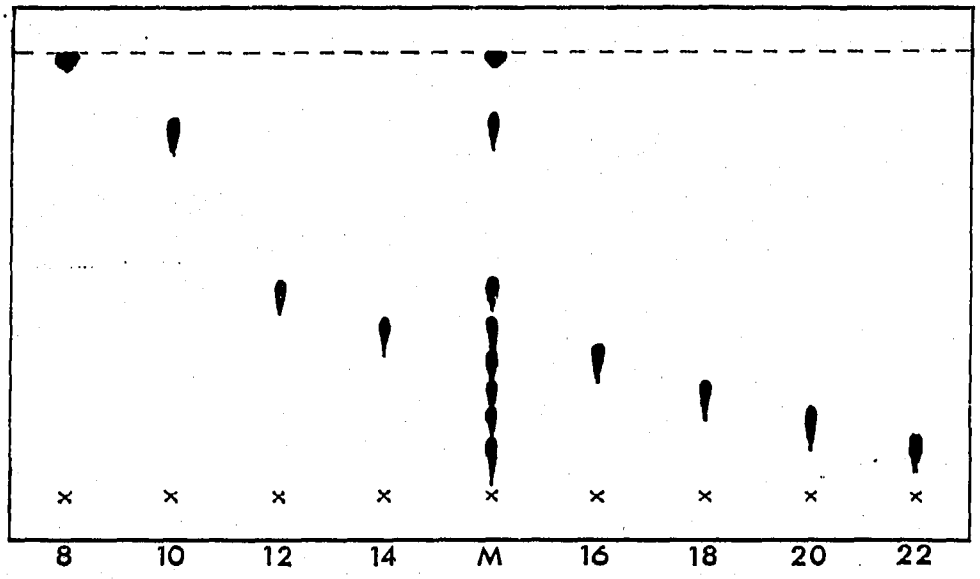

Fig. 2. Resolution of the *n*-acids by "adsorption" chromatography. The numerals indicate the number of carbon atoms in each acid. M is a mixture of all the test samples. (Substrate: kieselgur G. Solvent: cyclohexane. Chromogenic reagent: bromocresol green).

according to the period for which the kieselgur films had been allowed to dry. On films that had been dried by treatment at 110° for 30 min the R_F values were low and the resolution was poor. These observations suggest that partition, between the residual water in the kieselgur and the moving phase, makes an important contribution to the degree of resolution.

By continuous development, it was possible to obtain satisfactory resolution of a mixture of all the even-numbered fatty acids from *n*-decanoic to *n*-docosanoic on kieselgur G films which had been baked for 30 min at 110°. As before, cyclohexane was the developing solvent, but the development was performed in a tank fitted with the slotted li ! described by TRUTER[3]. The time required for development was 4 h and the distance from the front to the origin was 14 cm.

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SUMMARY

It is shown that "adsorption" chromatography on films of kieselgur G, using cyclohexane as the developing solvent, will resolve mixtures of the even-numbered, *n*-alcohols containing between ten and twenty-six carbon atoms per molecule within a distance of 10 cm. Resolution of similar mixtures of the *n*-acids under the same conditions is rather less satisfactory, but it is entirely satisfactory if the chromatogram is submitted to continuous development.

REFERENCES

1 H. P. KAUFMANN AND Z. MAKUS, *Fette, Seifen, Anstrichmittel*, 62 (1960) 1014.
2 E. STAHL, *Chemiker-Zeitung*, 82 (1958) 323.
3 E. V. TRUTER, *J. Chromatog.*, 14 (1964) 57.