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Peter Ilinov^a; S. I. Dimov^a

^a Department of Biochemistry, Institute of Nutrition, Medical Academy, Sofia, Bulgaria

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USE OF SOME SILVER SALTS OF AROMATIC SULFONIC ACIDS IN THIN-
LAYER CHROMATOGRAPHY

Peter Ilinov and S. I. Dimov
Institute of Nutrition, Medical Academy,
Department of Biochemistry,
15, Dimitar Nestorov St.,
1431 Sofia,
Bulgaria

SUMMARY

Some silver salts of aromatic sulfonic acids were used for thin-layer impregnation. The chromatographic properties of these salts were examined by separation of fatty acid methyl esters with different degrees of saturation as well as of their cis- and trans-isomers. Benzene sulfonic acid silver salt was more thoroughly investigated. An attempt was made to prove the effect of the anion of the different silver salts on the R_f values of a model mixture of fatty acid methyl esters.

INTRODUCTION

Silver nitrate has long been used for thin-layer separation of compounds according to the degree of saturation (1, 2, 3,

4, 5). Silver perchlorate and fluoroborate (6) as well as silver oxide (7), thallos nitrate (8) and silver sulfamate (9) have also been suggested for this purpose. Silver sulfamate has proven to be very suitable for separation of fatty acid cholesterol esters. The metallic ion (Ag, Pt, Pd, Tl) is thought to form a π -complex with compounds having double bonds. The stability of this complex depends on the number, type, geometry and position of the double bonds in the molecule of the compound. All this is used in certain chromatographic methods for separation of compounds according to the degree of saturation.

This paper deals with the possibility of use silver salts of aromatic sulfonic acids in thin-layer chromatography.

EXPERIMENTAL

Silver salts of the following aromatic acids were prepared:

Table 1

1. Benzenesulfonic acid (HO_3SAr)
2. 4-Methylbenzenesulfonic acid
3. 2,5-Dimethylbenzenesulfonic acid
4. 1-Naphtalenesulfonic acid
5. 2-Naphtalenesulfonic acid
6. 4-Hydroxybenzenesulfonic acid
7. 3-Carboxy-4-hydroxybenzenesulfonic acid
8. Sulfamic acid

Silver nitrate

All salts were prepared in a similar manner. The aqueous solution of the corresponding acid was neutralized with freshly precipitated silver oxide at room temperature. The silver salt crystallized out either on storing at room temperature or

on evaporation under vacuum. The concentration of the stock solutions was chosen according to the solubility of the silver salt to be obtained. For example, 6 g of benzenesulfonic acid was dissolved in 100 ml water and freshly precipitated silver oxide was added to the solution until complete neutralization. The consumed silver oxide was equivalent to about 7 g silver nitrate. The yield of silver benzenesulfonate was close to the theoretical one (97%). Silver benzenesulfonate represents leaf-like crystals with a melting point of more of 250 C which are very soluble in water and ethanol. Since some of the silver salts of the aromatic sulfonic acids are more slightly soluble in water, water and acetonitrile (4:1 v/v) were used as a solvent.

The silver salt of benzenesulfonic acid was first synthesized by Freund (1861) but by a different procedure.

Chromatographic System: 0,4 g (about 1,5 mmoles) of benzenesulfonic acid silver salt was dissolved in 5,5-6,0 ml distilled water. A mixture of 1,0 g Silica Gel G and 1,0 g Silica Gel HR (Merck) were slurried with this solution. Five glass plates (19 x 4 cm) were uniformly coated by means of spreader. Thickness is about 0,25 to 0,30 mm. The chromatographic plates were allowed to air-dry and kept in dry and dark until use. The model mixture of fatty acid methyl esters was prepared using lipid standard for chromatography (no 189-1, Sigma, St. Louis, Mo, USA) to which trans-oleic acid methyl ester and trans, trans-linoleic acid methyl ester were added. The concentration of the fatty acid methyl esters was about 2 mg/ml except for the trans, trans-linoleic acid methyl ester which was 1,0 to 1,3 mg/ml. Hexane was used as a solvent. From this solution 2 μ l dropwise or 20-25 μ l in a way of band was applied on the start.

Solvent System: Hexane-pentane-diethylether-acetic acid (100:30:6:3 v/v). Development time - about 30 min. Length of run - about

12 cm. Chamber volume/mobile phase volume ratio was 30:1. The development was carried out in a closed chamber at room temperature. Separation improved if a precooled plate was placed in the chamber.

After development of the chromatograms and evaporation of the solvent the plates were sprayed with 20% solution of sulfuric acid in water-methanol (3:2 v/v) and dried in an oven at 120 C for 10 min. The chromatograms were then placed over a heated (200 C) metallic plate for 10 min. Unsaturated fatty acids appeared as black spots on a white background. To obtain more intensive darkening of the spots of the saturated acids they were sprayed again with the sulfuric acid solution and the chromatograms were reheated. The spots could be successfully measured by densitometry.

RESULTS AND DISCUSSION

Fig.1 shows two chromatograms developed on a silver nitrate- and silver benzenesulfonate-impregnated layer. The silver ion concentration and all other conditions of development of the chromatograms were the same. The chromatograms demonstrate that silver benzenesulfonate allows for the separation of the critical pair cis-oleic acid/trans, trans-linoleic acid, which could not be achieved with silver nitrate only. The limit of detection was of the order of 0,8 to 1,0 μg for unsaturated acids and about 5,0 μg for saturated acids. The chromatographic plates impregnated with silver benzenesulfonate were more resistant to light and to mechanical damage as compared to those with silver nitrate. The Table 2 summarizes the R_f values obtained on a thin-layer impregnated with AgNO_3 and AgO_3SAR :

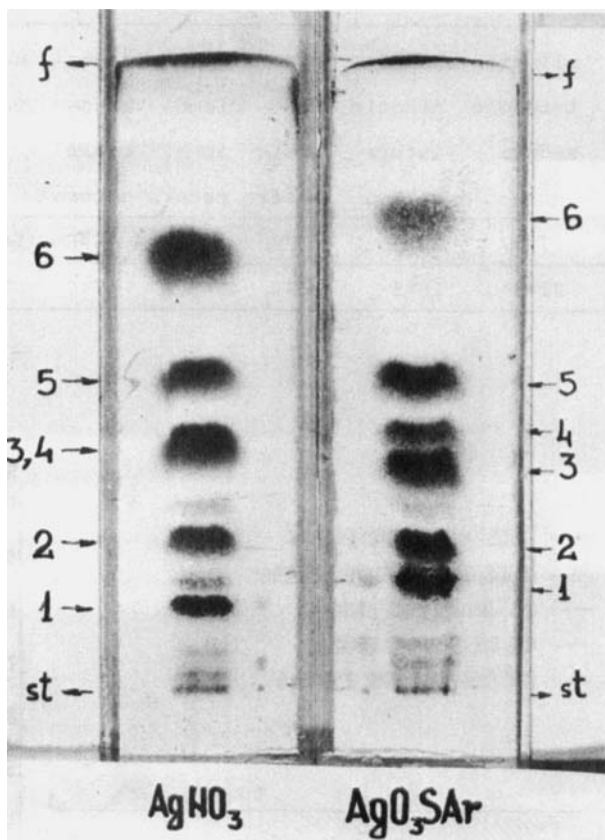


Fig. 1. Chromatography of the fatty acid methyl esters on silver nitrate and silver benzenesulfonate (AgO_3SAr) impregnated silica-gel layers:

1. all cis-trienoic esters
2. all cis-dienoic esters
3. cis-monoenoic esters
4. all trans-dienoic esters
5. trans-monoenoic esters
6. saturated esters

Table 2

 $R_f \times 100$ values of some fatty acid methyl esters (mean \pm SD)

Impregnated layer with	all cis-trienoic esters	all cis-dienoic esters	cis-monoenoic esters	trans-dienoic esters	trans-monoenoic esters	saturated
AgNO ₃	17 \pm 5	25 \pm 5	37 \pm 6	-	44 \pm 8	58 \pm 4
AgO ₃ SAr	21 \pm 3	28 \pm 5	36 \pm 6	40 \pm 5	47 \pm 6	67 \pm 4

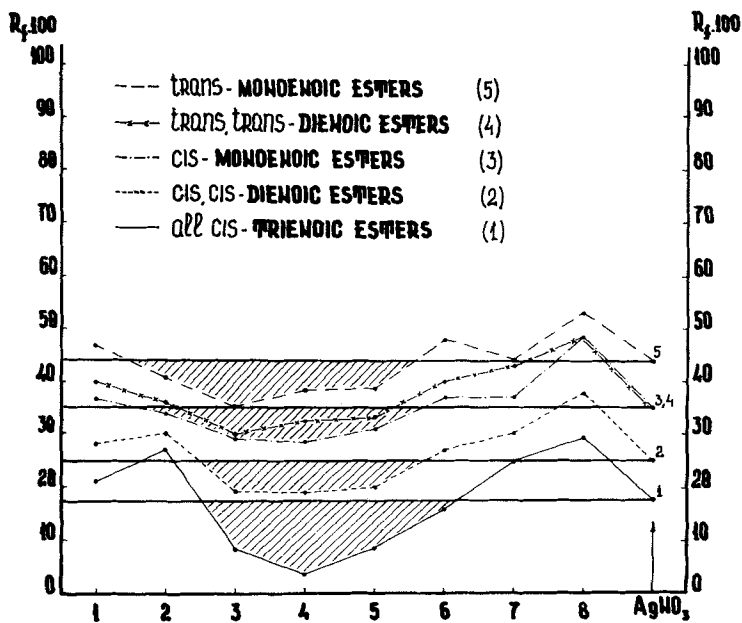


Fig. 2. $R_f \times 100$ values of 5 different fatty acid methyl esters. For numbers 1-8 see Table 1. The solid horizontal lines correspond to the R_f values obtained on AgNO₃-layer. The shaded areas express a greater stability of the π -complex, which can be attributed to the different chemical nature of silver salt anion.

Here again the silver ion concentration (about 1,5 mmoles) in the layer and the conditions of development of the chromatograms were the same. From Fig.2 it is clear that the stability of the π -complex depends not only on the number and geometry of the double bonds but also on the corresponding acid residue (anion) of the silver salt. This suggests that besides silver nitrate other silver salts could also be used for thin-layer separation of fatty acid methyl esters.

CONCLUSION

The proposed silver benzenesulfonate proved to be very suitable for separation of fatty acids with different degree of saturation as well as of their cis- and trans-isomers on thin-layer chromatographic plates. This chromatographic procedure could be used as a rapid and easy-to-perform method for control of the process of producing hydrogenated oils or for control of foods containing partially hydrogenated oils. The use of densitometry allows for the quantitative evaluation of the results.

REFERENCES

1. Barrett, C.B., M.S.J. Dallas and F.B. Padley (1962) Chem. Ind. (London), 1050-1051
2. Vries de B. and G. Yurriens (1963) Fette Seifen 65, 725-727
3. Morris, L.J. (1966) J. Lipid Res. 7, 717-732
4. Morris, L.J., R.T. Hollman and K. Fontelb (1961) J. Lipid Res. 2, 68-
5. Carreau, J.P. and J. Raulin (1965) Rev. Franc. de Corp. Gras. 12, 87-89

6. Morris, L.J., D.M. Wharry and E.W. Hammond (1967)
J. Chromatogr. 31, 69-75
7. Tabak, S., and M.R.M. Verzola (1970) J. Chromatogr.
51, 52, 334-338, 500-504
8. Baines, D.A. and R.A. Jones (1970) J. Chromatogr.
47, 130-132
9. Ilinov, P., (1979) Lipids 14, 598-600