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Received June 19th, 1967

J. Chromatog., 31 (1967) 551-556

Detection of rearrangement reactions by silver nitrate thin-layer chromatography

The method of separation and determination of triglycerides according to unsaturation and isomeric configuration on thin layers of silver nitrate impregnated silica gel is a recent elegant analytical development. Since the time that DE VRIES¹ had effected the separation of the methyl esters of palmitic, oleic, elaidic and linoleic acids and triglycerides like elaidodipalmitin and oleodipalmitin on a silicic acid column impregnated with silver nitrate, many investigators extended this method to silica gel thin layers containing silver ions in order to elucidate the compositions of natural, synthetic and modified triglycerides. BARRETT *et al.*² later adapted the silver nitrate thin-layer chromatography to the separation and estimation of constituent triglycerides of lard, interesterified lard, cocoa butter, palm oil, peanut oil, soybean oil and cottonseed oil. Subsequently REISER *et al.*³ and JURRIENS *et al.*^{4,6} utilised the thin-layer technique for quantitative analyses of natural triglycerides. KAUFMANN AND WESSELS⁵ separated the glycerides of sunflower oil by first fractionating on a silver nitrate impregnated silica gel layer and effecting further separation in a reversed phase system. PRIVETT *et al.*⁷ by adopting this method determined quantitatively the component glycerides formed by the random rearrangement reaction of a synthetic

J. Chromatog., 31 (1967) 556-559

mixture of tripalmitin, triolein and trilinolein as well as tripalmitin, triolein and trilinolenin, in conjunction with lipase hydrolysis.

The present report records the separations of triglycerides of some natural seed oils such as cottonseed, groundnut, sesame, mustard, safflower and linseed before and after a random rearrangement reaction on silver nitrate impregnated silica gel. The report is an extension of previous work done by us on the detection of the rearrangement reaction by reversed-phase paper and thin-layer chromatography techniques⁸.

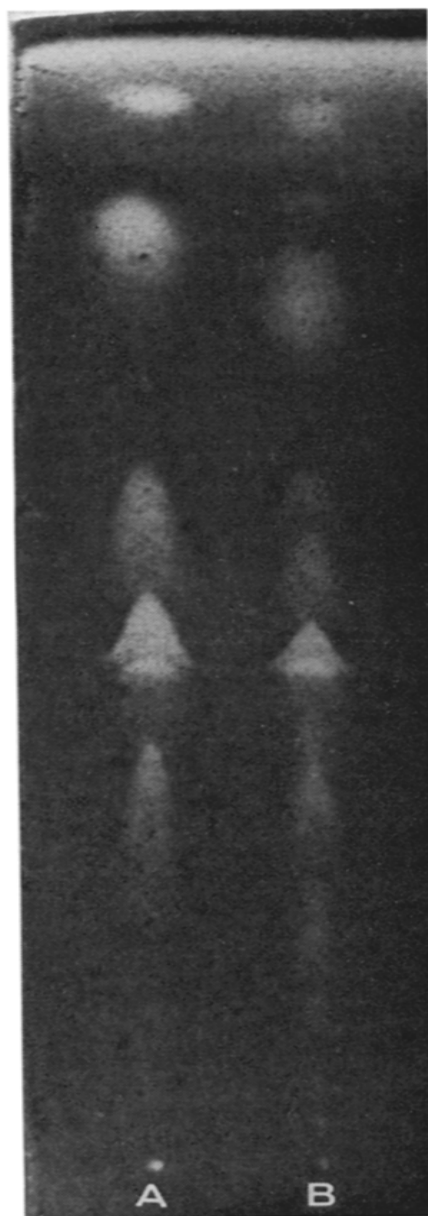
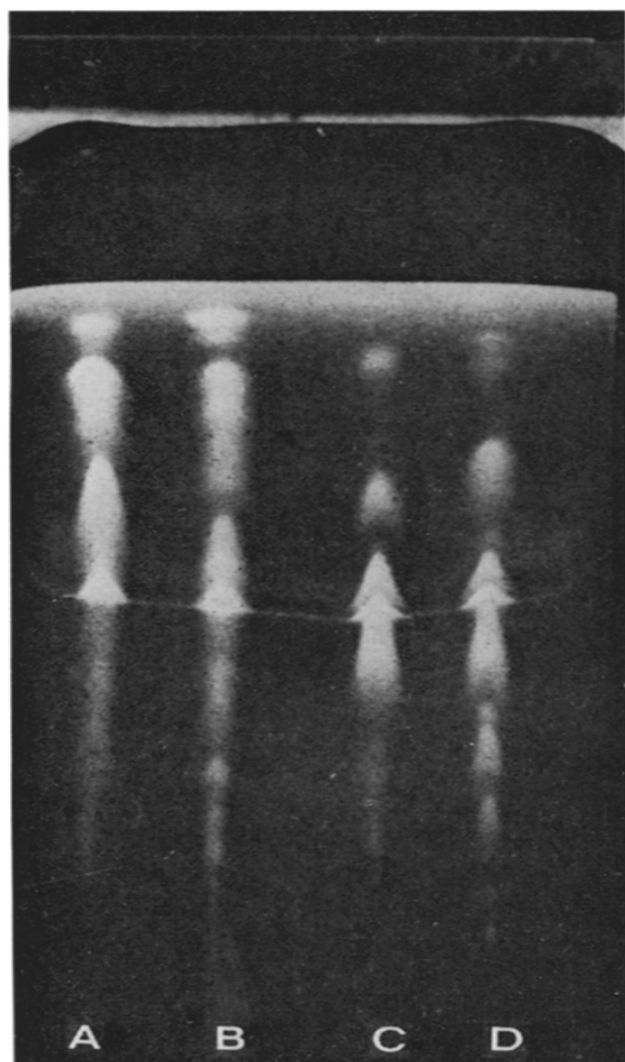


Fig. 1. Separation of mustard and safflower glycerides. (A) Natural mustard glycerides; (B) randomised mustard glycerides; (C) natural safflower glycerides; (D) randomised safflower glycerides. Solvent system: chloroform-acetic acid-methanol (99.0:0.5:0.5).

Fig. 2. Separation of cottonseed glycerides. (A) Natural cottonseed glycerides; (B) randomised cottonseed glycerides. Solvent system: chloroform-acetic acid-methanol (98.5:0.5:1.0).

Experimental

The plates were prepared by essentially following the method of BARRETT *et al.*² Glass plates (20 × 10 cm) were coated with a slurry of 8 g Silica Gel G (Merck) and 18 ml of 12.5% aqueous silver nitrate solution. For a plate of 40 × 10 cm the slurry was made from 16 g silica gel and 36 ml of a 12.5% aqueous silver nitrate solution. The plates were allowed to remain in air for 30 min to set the layers and afterwards baked at 110° for 1 h.

200 μg of the original and randomly rearranged triglyceride samples was spotted in the form of 1% solutions in chloroform (Merck). In the case of linseed oil glycerides the same amount was applied in the form of small bands on a long plate (40 × 10 cm).

The plates were eluted twice with chloroform (Merck) containing 0.5% acetic acid (A.R., B.D.H.) and 0.5, 1.0 and 2.0% of anhydrous methanol (Merck) depending

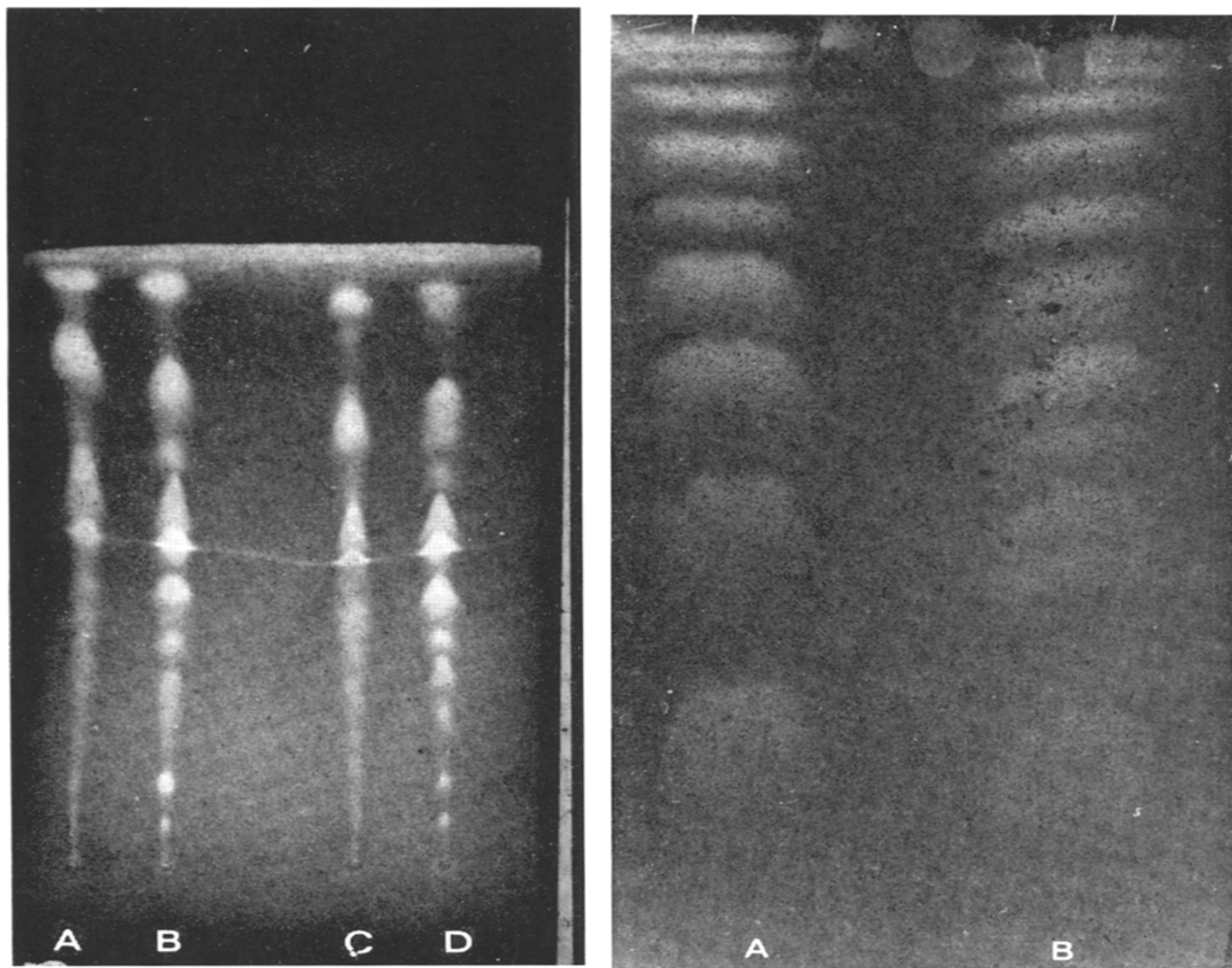


Fig. 3. Separation of groundnut and sesame glycerides. (A) Natural groundnut glycerides; (B) randomised groundnut glycerides; (C) natural sesame glycerides; (D) randomised sesame glycerides. Solvent system: chloroform-acetic acid-methanol (98.5:0.5:1.0).

Fig. 4. Separation of linseed glycerides. (A) Natural linseed glycerides; (B) randomised linseed glycerides. Solvent system: chloroform-acetic acid-methanol (97.5:0.5:2.0).

on the fatty acid composition of the original oils. After elution the plates were kept at about 110° for 10–15 min, cooled in a current of air and sprayed with a 0.1 % solution of 2,7-dichlorofluorescein in 95 % ethanol and finally viewed under U.V. light.

Discussion

The separations are shown in Figs. 1–4. They substantiate the earlier observation⁸ that the rearrangement reaction involving the principle of randomisation increases the number of component glycerides.

It may be pointed out that it was necessary in the case of linseed oil glycerides, original and rearranged, to carry out the separation on a long plate (40 × 10 cm) in order to detect the difference in their pattern of separation, which failed with a short plate (20 × 10 cm).

The silver nitrate method appears useful for ascertaining the alterations in glyceride compositions particularly in the case of highly unsaturated oils which exhibit very little changes in their physical properties after random rearrangement. The method also offers a better assessment of the rearrangement effect on glyceride compositions, for the resolution of glycerides obtained in most cases is more complete compared to the resolutions on reversed-phase paraffin impregnated kieselguhr plates obtained earlier by us.⁸ The technique should prove useful in studies involving ester interchange reaction of glycerides.

Investigations into further characterisation of the component glycerides of both original and rearranged seed oils by the present technique are in progress.

Acknowledgements

The authors are grateful to Dr. P. C. MAITI AND Mr. R. C. BANERJEE of Central Forensic Science Laboratory, Calcutta, for their help in photography. Grateful acknowledgement is also due to Dr. C. BANDYOPADHYAY for helpful suggestions.

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Received June 15th, 1967