CHROM. 4203

Analysis of phenyl esters of fatty acids, hydroxyphenyl alkyl ketones and long chain alkyl phenols by thin-layer chromatographic techniques

Alkyl phenols are important intermediates in many fields such as plastics, surface coatings, detergents, dyes, etc., and *p*-alkyl phenols are often used as additives to lubricating oils. Various physical methods such as ultra-violet spectroscopy and mass spectrometry are not very satisfactory for the identification of individual phenols in complex mixtures. Therefore rapid and efficient analytical techniques for the identification of alkyl phenols in the many preparations and formulations would be of great interest. Simple alkyl phenols have been separated by paper and thin-layer chromatographic techniques[1-6]. DIAMOND[7] achieved excellent separations of (C_2–C_{12}) *p*-alkyl phenols on thin layers of polyamide but this procedure was not satisfactory for the identification of higher homologues.

Ortho- and *para*-long chain alkyl phenols are conveniently prepared by the Fries rearrangement of the phenolic esters of fatty acids, separation of the two isomeric ketones so formed and their subsequent Clemmensen reduction. In this communication, the separation of (*n*-C_{12}–C_{18}) phenyl esters of fatty acids, hydroxyphenyl alkyl ketones and alkyl phenols by simple thin-layer chromatographic techniques is reported. These have been used to check the purity of the intermediates as well as the final products in the synthesis of *o*- and *p*-substituted (*n*-C_{12}–C_{18}) alkyl phenols later used for kinetic rate studies on their condensation with formaldehyde.

Experimental

Preparation of the materials. Lauric, myristic and palmitic acids (supplied by BDH) were further purified by crystallisation and fractional distillation. Stearic acid was prepared by the hydrogenation of pure oleic acid followed by crystallisation. Their purity was further checked by TLC.

The phenyl esters of the fatty acids were prepared by reacting phenol and the corresponding fatty acids together in equimolar proportions in the presence of *p*-toluenesulphonic acid as catalyst. Hydroxyphenyl alkyl ketones were obtained by subjecting the phenyl esters to the Fries rearrangement, followed by separation of the *o*- and *p*-keto isomers as a result of the preferential solubility of the *para*-isomer in 1–2 % aqueous alkali. The *o*- and *p*-alkyl phenols were then obtained by reducing the respective ketones by the Clemmensen reduction.

Thin-layer chromatographic techniques. TLC plates were prepared by spreading a slurry of Silica Gel G (EM, 30 g) in water (60 ml) over clean glass plates (20 × 20 cm) using a Camag applicator so as to obtain a layer of 250 μ thickness. The plates were activated by heating at 110° for 30 min.

Reversed-phase thin-layer chromatographic plates were prepared by developing the Silica Gel G plates in a chromatographic chamber with a 5 % silicone oil solution in ether in an ascending manner.

Ether solutions of the materials were spotted on the plates and the plates were developed with petroleum ether (40–60°)–ether for the Silica Gel G plates and acetic acid–water or acetonitrile–acetic acid–water for the reversed-phase plates. After the development, the chromatographic plates were air-dried, sprayed with chromic acid

solution and heated in an air oven at 120° for 2 h when the compounds showed as brown or black spots against the white background.

Results and discussion

Reversed-phase TLC clearly resolves homologous phenyl esters and alkyl phenols (Figs. 1 and 3) while silica gel TLC effectively separates isomeric hydroxyphenyl alkyl ketones and alkyl phenols (Fig. 2.) A combination of these two techniques has been found very useful in following the course of reactions in the synthesis of (n-C_{12}–C_{18}) alkyl phenols.

The separation of the phenyl esters of lauric, myristic, palmitic and stearic acids by reversed-phase TLC using acetic acid–water (80:20) as a solvent system for development, are shown in Fig. 1. All the four homologous phenyl esters are separable (items A, B, D and E). A similar pattern of results was obtained with the acetonitrile–acetic acid–water (70:10:20) system. The results also indicate that a few lower and higher homologues than those used in the present study may be separated by this technique.

The behaviour of the phenyl esters of lauric and stearic acids, on Silica Gel G, and their *o*- and *p*-hydroxyphenyl alkyl ketones and *o*- and *p*-alkyl phenols on using petroleum ether (40–60°)–ether– acetic acid (90:10:0.5) is shown in Fig. 2. Homologues of the phenyl esters of the fatty acids, and isomeric hydroxyphenyl alkyl ketones and alkyl phenols are not separable (items A and G; B and H; C and I; D and J; E and K). However, the phenyl esters are easily resolved from the corresponding *o*- and *p*-hydroxyphenyl alkyl ketones which in turn are separable from each other. Thus *o*-hydroxy laurophenone and *o*-hydroxy stearophenone are easily separable from their *p*-isomers

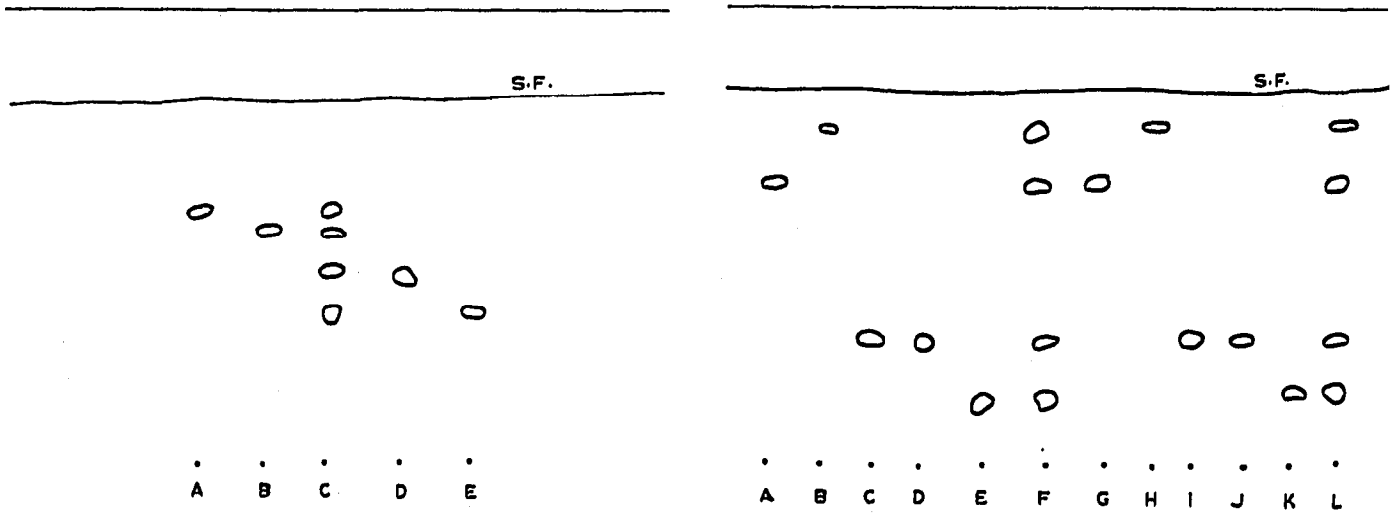

Fig. 1. Chromatogram of phenyl esters of fatty acids on silicone oil impregnated (reversed phase) Silica Gel G. Solvent system: acetic acid–water (80:20). A = Phenyl laurate, B = phenyl myristate; C = A + B + D + E; D = phenyl palmitate; E = phenyl stearate.

Fig. 2. Chromatogram of phenyl esters of fatty acids, *o*- and *p*-hydroxyphenyl alkyl ketones and *o*- and *p*-alkyl phenols on Silica Gel G. Solvent system: petroleum ether (40-60°)–ether–acetic acid (90:10:0.5) A = Phenyl laurate; B = *o*-hydroxy laurophenone; C = *p*-hydroxy laurophenone; D = *o*-dodecylphenol; E = *p*-dodecylphenol; F = A + B + C + D + E; G = phenyl stearate; H = *o*-hydroxy stearophenone; I = *p*-hydroxy stearophenone; J = *o*-octadecyl phenol; K = *p*-octadecyl phenol; L = G + H + I + J + K.

and from the corresponding phenyl esters (items A, B and C; G, H and I). Fig. 2 also shows the separation of *o*- and *p*-alkyl phenols from each other (items D and E; J and K) and from the corresponding hydroxyphenyl alkyl ketones and phenyl esters (items A, B and D; A, C and E; G, H and J; G, I and K). The *o*-isomers have higher migration characteristics than the *p*-isomers (Table I).

TABLE I

R_F VALUES OF PHENYL ESTERS OF FATTY ACIDS, HYDROXYPHENYL ALKYL KETONES AND ALKYL PHENOLS

Compound	*Silica Gel G** ($R_F \times 100$)	*Reversed-phase*** ($R_F \times 100$)
Phenyl laurate	76	70
Phenyl myristate	75	65
Phenyl palmitate	76	53
Phenyl stearate	75	42
o-Hydroxy laurophenone	90	—
o-Hydroxy stearophenone	90	—
p-Hydroxy laurophenone	34	—
p-Hydroxy stearophenone	34	—
o-Dodecyl phenol	32	70
o-Tetradecyl phenol	32	65
o-Hexadecyl phenol	31	53
o-Octadecyl phenol	32	42
p-Dodecyl phenol	17	71
p-Tetradecyl phenol	16	66
p-Hexadedyl phenol	17	54
p-Octadecyl phenol	17	42

* Petroleum ether (40–60°)–ether–acetic acid (90:10:0.5).
** Acetic acid–water (80:20).

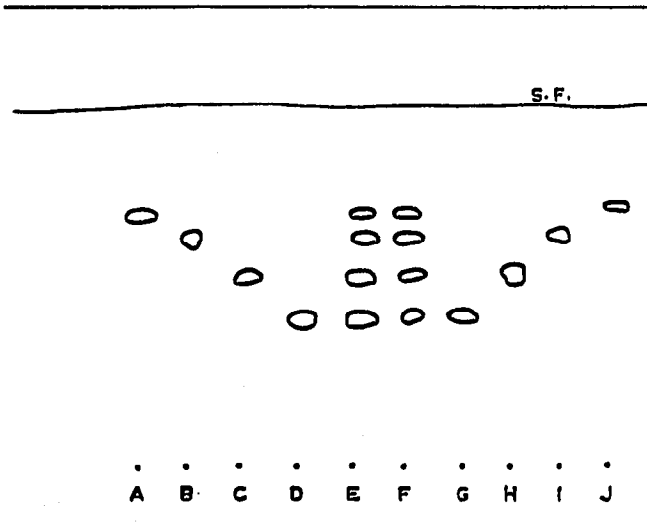

Fig. 3. Chromatogram of *o*- and *p*-alkyl phenols on silicone oil impregnated (reversed phase) Silica Gel G. Solvent system: acetic acid–water (80:20). A = *o*-Dodecyl phenol; B = *o*-tetradecyl phenol; C = *o*-hexadecyl phenol; D = *o*-octacedyl phenol; E = A + B + C + D; F = G + H + I + J; G = *p*-octadecyl phenol; H = *p*-hexadecyl phenol; I = *p*-tetradecyl phenol; J = *p*-dodecyl phenol.

Silica gel TLC does not throw any light on the homogeneity of individual *o*- or *p*-alkylphenols having different chain lengths. However, reversed-phase TLC, with the solvent system acetic acid–water (80:20), separates the *o*- or *p*-alkyl phenol homologues due to the difference in the chain length of the alkyl groups. Fig. 3 shows that this technique effectively separates dodecyl, tetradecyl, hexadecyl and octadecyl phenols among the *ortho* or *para* class of compounds (items A, B, C and D; G, H, I and J) but does not distinguish isomeric alkyl phenols (items A and J; B and I; C and H; D and G) which can be separated only by silica gel TLC (Fig. 2). These separations also indicate that resolution of some of the lower and higher homologues is possible. This method is useful in determining their purity. The results of all the separations are summarised in Table I.

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Simple and rapid polyamide chromatography of antioxidants

The use of paper or thin-layer chromatography for the identification of antioxidants had been widely discussed[1–3]. A simple and rapid method for the analysis of antioxidants by polyamide layer chromatography is presented in this note. The results described are obtained with universally used spray reagents and two developing solvent systems.

Experimental

Chemicals. Eight kinds of antioxidant of F.D.A. standard were used. The solvents and chemicals are the first grade of Katayama Chemical Industries, Ltd., Osaka, Japan.

Thin-layer sheets. All the polyamide thin-layer sheets used were 15 × 15 cm and produced by Cheng Chin Trading Co. Ltd., Taipei, Taiwan.

Chromatography. The standard techniques of ascending thin-layer chromatography[4] was employed. The solvent systems were: petroleum ether (30–70°)–benzene–acetone (8:2:5) and acetone–ethyl alcohol–water (4:1:2).