CHROMATOGRAPHIC INVESTIGATION OF FATTY ALCOHOLS

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Fatty alcohols obtained either from natural sources, *e.g.* wax, whale oil, sperm oil etc., or synthetically by oxidation of the paraffins to fatty acids followed by high pressure hydrogenation as well as by oxo-synthesis have been found to be useful raw materials for synthetic detergents. Chemical intermediates and derivatives of fatty alcohols, *e.g.* of oleyl alcohol, have proved to be useful as lubricants and plasticizers[1].

Before the advent of chromatography the systematic study of fatty alcohols was mainly based on their physico-chemical characteristics, *e.g.* refractive index, boiling point, melting point, hydroxyl value etc. During the past few years the immense development of chromatographic techniques has led to better separation and more precise characterisation of fatty alcohols irrespective of their origin.

Separation of lower molecular weight fatty alcohols in the form of different derivatives, *e.g.* as xanthogenate[2], 3,6-dinitro-phthalic acid ester[3], with the help of paper chromatography was reported. KAUFMANN AND KOHLMEYER[4] separated C_{12}–C_{18} fatty alcohols on undecane impregnated paper using acetic acid as the mobile phase. The spots were identified by spraying the chromatogram with rhodamine B. The separation of higher alcohols from C_{16} to C_{30} as mercuric allyl urethane derivatives has been achieved by KAUFMANN *et al.*[5].

Recently thin layer chromatography emerged as a useful tool for the successful separation of fatty alcohols. KAUFMANN AND DAS[6] were able to separate higher alcohols (C_{16}–C_{26}) obtained from different natural and synthetic waxes on tetradecane impregnated Silica Gel G plates with isopropyl alcohol–acetic acid–ethyl alcohol–water (8:4:3:2) as solvent either at room temperature or at 42–43° depending upon the chain length. The spots were then identified with the help of rhodamine B solution. Higher aliphatic alcohols from C_{10} to C_{18} were identified and separated by HASHIMOTO and co-workers[7] on paraffin impregnated Silica Gel G plates using solvent systems such as petroleum ether–diethyl ether (4:1); hexane–diethyl ether (7:3); hexane–diethyl ether–acetic acid (7:3:0.1) and xylene–diethyl ether (4:1). In this way unsaponifiables from wool wax, sperm oil and beeswax were evaluated. Thin layer chromatographic separation of monoenoic, dienoic and trienoic fatty alcohols, in the form of mercuric acetate derivatives on silver nitrate impregnated Silica Gel G plates, was studied by HASHIMOTO *et al.*[8] using petroleum ether–diethyl ether (80:20), propyl alcohol–acetic acid–pyridine (150:1:1), diisobutyl ketone–acetic acid (40:10) as solvents. Relatively few investigations of fatty alcohols by means of gas–liquid chromatography have been reported[9,10].

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The object of the present work was to develop a simple and rapid thin layer chromatographic method for the separation and identification of fatty alcohols having a chain length ranging from C_8 to C_{22} as such, as well as fatty alcohol acetates.

EXPERIMENTAL

Synthetic fatty alcohols (commercial) and the sperm oil alcohols used in the investigation were obtained from the firm M/S Otto Aldag, Hamburg-Bergedorf, West Germany. Test substances such as pure C_8 to C_{20} saturated even-numbered straight chain fatty alcohols, commercially designated as "Alfol", were obtained from the firm M/S Condea A.G., Hamburg, West Germany.

The thin layer plates of Silica Gel G (E. Merck) and Kieselguhr G (E. Merck) respectively were prepared according to the usual method using a Desaga applicator[11].

Preparation of fatty alcohol acetates

Fatty alcohol acetates were prepared by heating 20 g fatty alcohol with 200 g acetic anhydride on a water bath at 90–95° for 2 h. It was then treated with 400 ml hot water so that the acetate separated as a layer. This layer was washed with hot water several times until the wash water was free from acetic acid. Finally the alcohol acetate was dried over anhydrous sodium sulphate and filtered.

The purity of the product thus obtained was verified each time and in each case by thin layer chromatography using Silica Gel G plates and petroleum ether–diethyl ether–acetic acid (85:15:1)[12] as solvent and the chromatogram was visualised by spraying with 50 % sulphuric acid followed by charring.

Acid value, saponification value, iodine value (Wijs' method), hydroxyl value and solidification point of fatty alcohols under investigation were determined by standard methods[13].

Thin layer chromatography of fatty alcohols

The Kieselguhr G plates were impregnated with a 10 % solution of liquid paraffin (Dickflüssig, E. Merck) in petroleum ether (b.p. 40–60°) and kept in the air for 15 min to remove the petroleum ether. 10–50 μg of fatty alcohols (as a 1 % solution in benzene; E. Merck) were spotted at a distance of 2 cm from the edge of the plate, the plates were then developed in a closed chamber containing acetone–water (75:25) as solvent, 80 % of which was previously saturated with the above liquid paraffin. After 1 h 40 min development time the plates were taken out of the chamber, heated for 10–15 min at 110° to remove the solvent, cooled and sprayed with a 1 % alcoholic solution of phosphomolybdic acid. The chromatograms were visualised by heating the plates at 110° in an oven when within 10–15 min white spots (in case of saturated fatty alcohols) or bluish violet spots (in case of sperm oil alcohols), appeared against a greenish background. Fig. 1 illustrates the separation of fatty alcohols.

Chromatography of fatty alcohol acetates

The fatty alcohol acetates in the form of 1 % solutions in benzene were placed on paraffin impregnated Kieselguhr G plates as described above. The solvent system used in this case was a mixture of acetone and water in the ratio of 90:10, 80 % of which was saturated with liquid paraffin. After single development (45 min) the

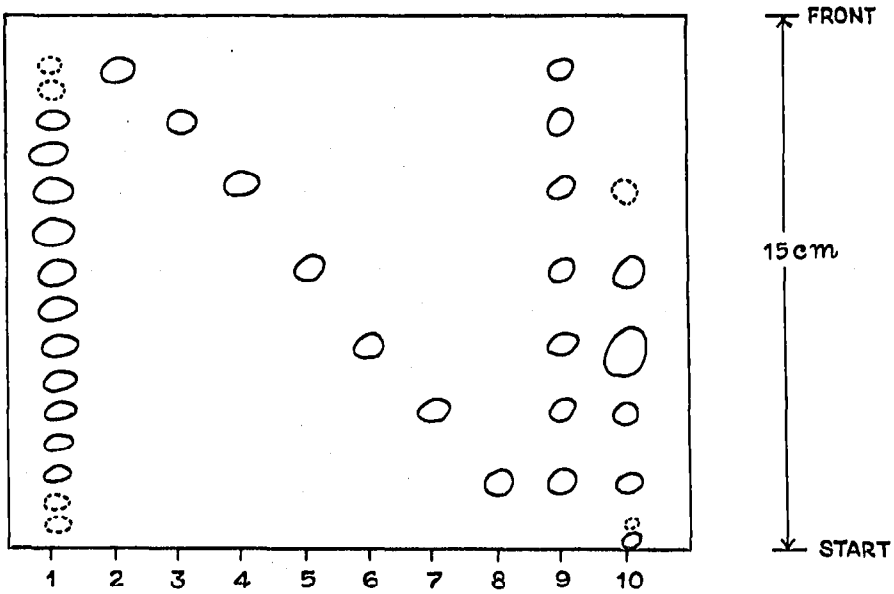

Fig. 1. Chromatographic separation of fatty alcohols. 1 = Commercial synthetic fatty alcohols; 2 = octyl alcohol; 3 = decyl alcohol; 4 = lauryl alcohol; 5 = myristyl alcohol; 6 = palmityl alcohol; 7 = stearyl alcohol; 8 = arachidyl alcohol; 9 = mixture 2–8; 10 = sperm oil alcohols.

solvent was removed from the plates by blowing a stream of nitrogen on to the surface of the plate and the plates were again developed in the same solvent. The chromatograms after double development were visualised by spraying with an alcoholic solution of phosphomolybdic acid as in the case of fatty alcohols. Fig. 2 shows the separation of fatty alcohol acetates.

Gas–liquid chromatographic investigation of synthetic fatty alcohols in the form of acetate derivatives was also carried out to determine the composition of

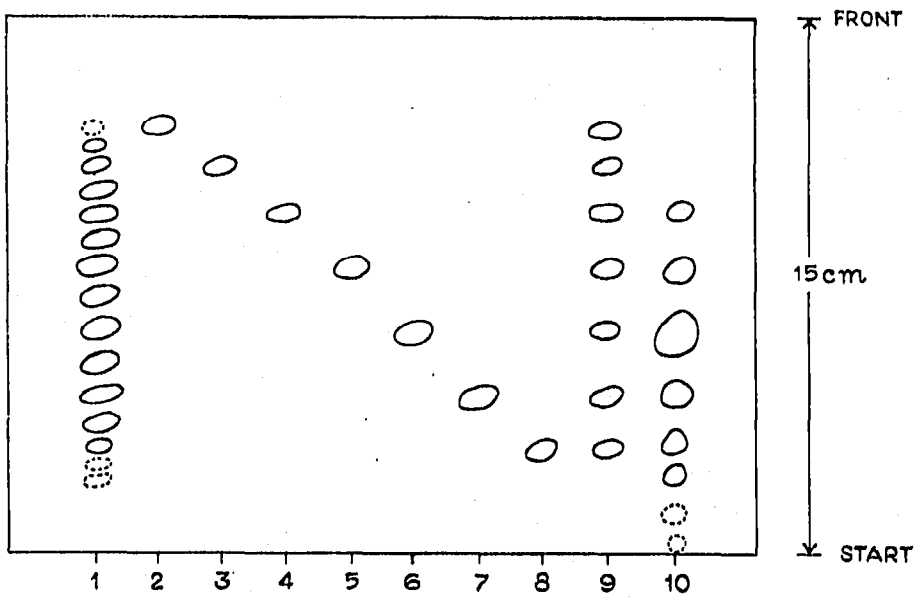

Fig. 2. Chromatographic separation of fatty alcohol acetates. 1 = Commercial synthetic fatty alcohol acetates; 2 = octyl alcohol acetate; 3 = decyl alcohol acetate; 4 = lauryl alcohol acetate; 5 = myristyl alcohol acetate; 6 = palmityl alcohol acetate; 7 = stearyl alcohol acetate; 8 = arachidyl alcohol acetate; 9 = mixture 2–8; 10 = sperm oil alcohol acetates.

commercial synthetic fatty alcohols. The apparatus used was a Beckman GC-2A model with a thermal conductivity detector. An 8 ft. × 1/4 in. stainless steel tube was packed with 10 % diethylene glycol succinate polyester on 60–80 mesh Chromosorb W and used at a column temperature of 200°. Gas flow was 96 ml of H_2 per min and current applied was 180 mA. The results were graphically recorded by a recorder (Bristol Strip Chart Recorder) and subsequently integrated by an integrator and finally expressed as % by weight of total fatty alcohol acetates calculated from areas under the curves in the chromatograms. The retention times of known fatty alcohol acetates were compared with the alcohol acetates from synthetic alcohols.

RESULTS AND DISCUSSION

The acid value, saponification value, iodine value, hydroxyl value and solidification point of commercial synthetic fatty alcohols and of sperm oil alcohols are given in Table I.

TABLE I

ANALYSIS OF COMMERCIAL SYNTHETIC FATTY ALCOHOLS AND OF SPERM OIL ALCOHOLS

	Synthetic fatty alcohols	*Sperm oil alcohols*
Acid value	Nil	Nil
Saponification value	Nil	Nil
Iodine value (Wijs)	0.5	65
Hydroxyl value	272.0	200.0
Solidification point	25°	21°

Table II indicates the composition of sperm oil alcohols and commercial synthetic fatty alcohols as determined by gas–liquid chromatography.

A comparative study of the gas–liquid chromatographic separation and thin layer chromatographic separation of synthetic fatty alcohols revealed that practically all the components, both even and odd chain length, present in the mixture can be successfully separated and identified by the present method of thin layer chromatography. The components below 1 % can, however, also be detected by increasing the amount of the substance to be spotted on the plate. From the nature and intensity of the spots the quantity of the fatty alcohol components in the mixture can be qualitatively assessed.

The synthetic fatty alcohol acetates, also have the same sequence of separation as shown in Fig. 2 compared to that of fatty alcohols in Fig. 1. The separation of the alcohol acetates, however, requires a higher proportion of acetone.

The chromatograms of sperm oil alcohols as such or in the form of acetates as shown in Figs. 1 and 2, respectively, show that the sperm oil alcohols are completely devoid of odd numbered fatty alcohols; this result is also supported by the gas–liquid chromatographic analysis (Table II). The variation in the number of components of the sperm oil alcohols detected by the gas–liquid and thin layer chromatographic techniques may be attributed to the presence of "critical pairs" appearing in thin

TABLE II

GAS–LIQUID CHROMATOGRAPHIC ANALYSIS OF FATTY ALCOHOLS

Fatty alcohol component	*Sperm oil alcohols** (% *composition by wt.*)	*Commercial synthetic fatty alcohols* (% *composition by wt.*)
C_7	—	0.9
C_8	1.8	2.0
C_9	—	4.6
C_{10}	1.4	7.7
$C_{10:1}$	1.0	—
C_{11}	—	9.4
C_{12}	3.9	9.8
$C_{12:1}$	1.9	—
C_{13}	—	9.4
C_{14}	17.1	9.4
$C_{14:1}$	6.8	—
C_{15}	—	8.9
C_{16}	19.0	8.0
$C_{16:1}$	15.5	—
$C_{16:2}$	3.7	—
C_{17}	—	6.6
C_{18}	5.0	5.9
$C_{18:1}$	22.1	—
$C_{18:2}$	4.0	—
C_{19}	—	5.1
C_{20}	—	4.2
$C_{20:1}$	6.1	—
C_{21}	—	3.6
C_{22}	—	2.5
$C_{22:1}$	0.7	—
C_{23}	—	2.0

* The analysis of sperm oil alcohols by gas–liquid chromatography was carried out by the Lurgi-Laboratory, Frankfurt, West Germany.

layer chromatography. For complete separation of sperm oil alcohols or their acetate derivatives, this method can be combined with the use of the recently developed silver nitrate plates, or two dimensional chromatography involving bromination and hydrogenation on the plate[14] might be adopted, although the present method gives an indication of their qualitative evaluation.

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SUMMARY

A simple thin layer chromatographic technique for the separation and identification of natural and synthetic fatty alcohols as such or in the form of their acetates on paraffin impregnated Kieselguhr G plates using acetone–water in proportions of

75:25 and 90:10, respectively, has been developed. Using this technique it was possible to detect alcohols or acetates from C_8 to C_{22} having even and odd chain lengths. The composition of the said fatty alcohols has also been determined by gas–liquid chromatography.

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