Paper Chromatography of Resin Acids

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Several methods of separating and identifying resin acids have been described in the literature. Many of these acids have been obtained in a pure state by fractional crystallisation of their salts with various amines [1,2]. This preparatively important method is however, tedious and less suited for analytical purposes. Partition chromatography has been employed by several workers [3,4], but a satisfactory separation of pimaric, isopimaric, sandaracopimaric ("crytopimaric") [5] and abietic acids has not been obtained [4]. Vapour phase chromatography [6] and mass spectrometry [7] have recently been used in examinations of the methyl esters of resin acids. Vapour phase chromatography suffers, however, from the disadvantages that several stationary phases have to be used and that methyl levopimarate and methyl palustrate are partly isomerised to methyl abietate and methyl dehydroabietate at the high temperatures required. This thermo-lability does not effect the latter method and analysis of mass spectra with the aid of a computer has been found to give good information on the nature of such mixtures [7].

A simpler method is, however, desirable. Wickberg [8] has recently developed a rapid and convenient method for the separation of unsaturated hydrocarbons by partition of their silver complexes between hexadecane and aqueous methanol and this method has now been applied to the methyl esters of resin acids. Methanolic solutions of the esters were applied to fibreglass paper impregnated with hexadecane and the chromatograms were developed with a solution of silver fluoborate [8,9] in aqueous methanol. The compounds were detected by immersing the partially dried paper in a 10 % solution of antimony pentachloride in chloroform. They appeared as round or slightly oval spots. The initial colour of the spots (see Table 1) darkened and intensified when the paper was heated at 100° for a few minutes. The total time required for the separation did not exceed 2 h.

The best results were obtained with a 25–30 % solution of silver fluoborate in ca 80 % aqueous methanol and are given in Table 1. The speed increased but the separation deteroriated when the methanol content was increased. Tailing occurred when the water content was increased and the paper became very brittle when the concentration of silver fluoborate exceeded 30 %. The R_F-values vary somewhat with the distance between the front and the starting line and it is, therefore, advisable to run a complete set of test substances when identifying the components of a mixture.

The increase in R_F-values of the esters containing two conjugated double bonds is found to parallel the increase in wavelength of the ultraviolet absorption maxima of the corresponding acids. Furthermore sandaracopimarate and isopimarate, which possess equatorially oriented vinyl groups, have higher R_F-values than pimarate possessing an axially oriented vinyl group. In a blank experiment it was shown that levopimarate, the most sensitive of the acids used, could be recovered unchanged,

Table 1. R_F-Values of methyl esters of resin acids on hexadecaneimpregnated paper eluted with A (25 g $AgBF_4$, 79 ml MeOH, 16 ml H_2O) and with B (30 g $AgBF_4$, 74 ml MeOH, 19 ml H_2O). Distance front-starting line ca. 130 mm.

Methyl esters	A	B	Colour	λ_{max} of corresponding acids, mμ [4]
Dehydroabietate [10,11]	0.15	0.06	Grey	
Abietate [11,12]	0.22	0.10	Red-brown	240–241
Neoabieatate [11,13]	0.33	0.13	Grey	250–252
Palustrate [11,14]	0.45	0.26	Yellow-brown	265–266
Levopimarate [11,15]	0.53	0.36	Red	272
Pimarate [11,16,17]	0.59	0.45	Grey	
Sandaracopimarate [5,17]	0.68	0.58	Dark grey	
Isopimarate [18,19]	0.68	0.58	Dark grey	

Table 2. R_F-Values of the resin acids on DMS-impregnated paper using light petroleum (b.p. 60 – 71°) as mobile phase.

Acids	R_F-value	
	Dry	Moist
Dehydroabietic	0.35	0.74
Abietic	0.52	0.87
Neoabietic	0.47	0.87
Palustric	0.53	0.90
Levepimaric	0.52	0.89
Pimaric	0.59	0.93
Sandaracopimaric	0.53	0.89
Isopimaric	0.51	0.89

which excludes rearrangement of the double bonds.

An attempt was made to separate the free acids by a method recently developed in this laboratory for the separation of certain carboxylic acids on dimethyl sulphoxide (DMS) impregnated paper [20]. The acids were applied as ether solutions and the chromatogram was developed with light petroleum. They migrated as almost circular spots and, as previously noted for aliphatic acids, the R_F-values were sensitive to the presence of moisture. The separation of the acids, as shown in Table 2, is less satisfactory than that obtained on partition of the silver complexes of their esters. The range within which these R_F-values appear permits simultaneous detection of co-occurring fatty acids of higher molecular weight than myristic acid or of lower molecular weight than nonanic acid [20].

Hexadecane-silver fluoborate-aqueous methanol system. The fibreglass paper (Schleicher and Schüll, 0.17 – 0.23 mm) was cut into strips 23 cm long with the starting line 5 cm from the upper end.

The papers were drawn at an even rate through a 10 %, v/v, solution of hexadecane in light petroleum (b.p. 60 – 71°), uniformly blotted between sheets of filter paper and dried under an infrared lamp.

Ca. 4 % solutions of the methyl esters in methanol were applied to the paper with the aid of a small capillary. The spots were placed 1.5 cm apart and at least 2 cm from the edge of the paper.

The chromatograms were developed by the descending technique using a mixture of (A) 21 ml of a 6 M aqueous solution of silver fluoborate and 79 ml of methanol or of (B) 26 ml of the silver fluoborate solution and 74 ml of methanol as mobile phase. The tank was saturated with a mixture of methanol and water (4:1). All solvents used for development and impregnation were of reagent grade. Freshly prepared solutions of the esters and of the eluent were used on each occasion. The chromatograms were run in the dark to avoid decomposition of the silver solutions.

The papers were partially dried under an infrared lamp and then drawn through a 10 % solution of antimony pentachloride in chloroform. The substances appeared as round or slightly oval spots which became darker and more intense when warmed on a hot plate at 100°.

Stability of methyl levopimarate in the eluting phase. A solution of methyl levopimarate in 30 % silver fluoborate in 80 % methanol-water was allowed to stand in a dark cupboard for 4 h. The solution was then diluted with water and the ester was extracted with ether. The recovered methyl levopimarate had m.p. 61 – 63.5° mixed m.p. 64 – 65° with an authentic sample (m.p. 64 – 65°).

Dimethyl sulphoxide-light petroleum system. The method used was identical to that given by Hammarberg and Wickberg [20]. The acids were applied in 2 – 5 % solution in dimethyl ether. The spots were detected by exposing the paper to ammonia vapour followed by spraying with Duncan and Porteous's indicator solution; the spots appeared light yellow on a green background and were stable for about 3 min.

Acknowledgements. We thank Prof. H. Erdtman for his kind interest and Mrs. S. Strand for skilful assistance. Thanks are also due to the *Swedish Technical Research Council* for financial support.

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Received July 2, 1962.

The Hydrolysis of 1,3-Dioxolan and Its Alkyl Derivatives. Part II. The Three Geometric Isomers of 2,4,5-Trimethyl-1,3-dioxolan

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In continuation of the previous study of the influence of structure on the kinetics of hydrolysis of derivatives of 1,3-dioxolan [1], the present paper describes the synthesis of, and kinetic data for the three geometric isomers of 2,4,5-trimethyl-1,3-dioxolan.

Experimental. The 2,3-butanediol employed in the synthesis of the examined dioxolans was a technical product (L. Light & Co., Ltd.) consisting mainly of the *meso* form. The *dl*-form present as an impurity was removed by careful distillation in a Todd precision fractionation assembly. Only the middle distillate, which crystallized in the receiver (b.p. 82—84°C/8 mm Hg; $n_D^{25} = 1.4370$), was employed in the subsequent syntheses. The pure *meso*-2,3-butanediol could be employed directly for the preparation of two geometric isomers of 2,4,5-trimethyl-1,3-dioxolan, but the *dl*-2,3-butanediol required in the synthesis of the third isomer was obtained from the *meso* form by the following reaction sequence:

$$\textit{meso}\text{-2,3-butanediol} \xrightarrow{Ac_2O} \textit{meso}\text{-2,3-butanediol diacetate} \xrightarrow{HBr} \textit{dl}\text{-2,3-dibromobutane} \xrightarrow{\text{Ag acetate}} \xrightarrow{\text{alkaline hydrolysis}} \textit{dl}\text{-2,3-butanediol}$$

The diacetate of *meso*-2,3-butanediol and *dl*-2,3-dibromobutane were prepared as described by Wilson and Lucas [2], whereas the preparation of *dl*-2,3-butanediol diacetate and *dl*-2,3-butanediol took place in principle by the method described by Winstein and Buckles [3]. All the intermediates and the final product *dl*-2,3-butanediol (b.p. 80°C/5 mm Hg) were carefully purified by fractional distillation.

The isomers of 2,4,5-trimethyl-1,3-dioxolan were prepared from acetaldehyde *n*-amyl acetal and the 2,3-butanediols by a procedure similar to that used to prepare 2,4-dimethyl-1,3-dioxolans [1]. The 2,*cis*-4,*trans*-5-trimethyl-1,3-dioxolan obtained from *dl*-2,3-butanediol had the following physical constants: b.p. 103.2°C/749.9 mm Hg, $n_D^{25} = 1.3922$, $d_4^{25} = 0.8894$, $[R]_{obs.} = 31.11$ ($[R]_{calc.} = 30.84$).

When *meso*-2,3-butanediol was the starting material, a mixture of 2,*cis*-4,*cis*-5-trimethyl-1,3-dioxolan and 2,*trans*-4,*trans*-5- trimethyl-1,3-dioxolan resulted. The components of the mixture were separated by careful fractional distillation. The physical properties of the lower-boiling component, which was the 2,*cis*-4,*cis*-5-form on the basis of kinetic and other data, were b.p. 109.5°C/751.0 mm Hg, $n_D^{20} = 1.4007$, $d_4^{20} = 0.9123$, $[R]_{obs.} = 30.91$ ($[R]_{calc.} = 30.84$) and those of the higher-boiling component, 2,*trans*-4,*trans*-5-trimethyl-1,3-dioxolan, b.p. 112.4°C/753.4 mm Hg, $n_D^{20} = 1.4038$, $d_4^{20} = 0.9201$, $[R]_{obs.} = 30.87$ ($[R]_{calc.} = 30.84$). The purities of the synthesized 2,4,5-trimethyl-1,3-dioxolans were checked by gas-chromatographic analysis.

The kinetic measurements were carried out as described previously [1].

The rate coefficients of the acid-catalyzed hydrolysis of the three isomers and kinetic quantities calculated from them are shown in Table 1. The assignations of the structures of the isomers were made on the