

TABLE II  
 DISPERSION EQUATION CONSTANTS AT 25°

	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> D <sub>6</sub>	C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> D <sub>12</sub>
Eq. 1 $\lambda^*$ , $\mu$	0.12929	0.14981	0.09418	0.09594
$C \times 10^{-13}$	6.858	5.978	3.779	3.538
$n_{\infty}$	1.47417	1.47369	1.41197	1.40813
$\nu_0 + 10^{-16}$	2.18632	2.10355	2.91743	2.97928
Eq. 2 $C \times 10^{-30}$	5.629058	5.155144	8.471202	8.733591
$\eta_{\infty}$	1.47568	1.47140	1.41254	1.40853

ment with the values given by Forziati<sup>2</sup> even though the values calculated in this research are from measurements made at a combination of wave lengths which are different than those used in the calculations by Forziati. The Hartmann equation reproduces the data with an error of about  $\pm 0.00002$  refractive index unit. The Sellmeier-Drude equation reproduces the data with an error of about  $\pm 0.0004$  refractive unit.

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### Cellulose Sheets as Chromatographic Supports<sup>1,2</sup>

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During our studies of the various techniques of partition chromatographic analysis<sup>3-7</sup> we have made extensive use of filter papers (*e.g.*, Whatman

No. 3)<sup>8</sup> for the separation of relatively large amounts of mixtures of sugars containing mono-, di-, tri- and tetrasaccharides but they have a limited loading capacity.<sup>9,10</sup>

In an extension of this work it has been found that limited use can be made of cellulose sheets,<sup>11</sup> approximately one-eighth of an inch thick, as chromatographic supports for bringing about the separation of a relatively large amount of a mixture of sugars. Due to the poor wet strength of this type of support, which is made from cellulose of short fiber length, it was necessary to carry out the development of the chromatograms in a horizontal direction. For these preliminary experiments a horizontal glass tube, 100 mm. diameter and closed at each end with a rubber stopper covered with aluminum foil, served as the chromatographic chamber and glass T-pieces, inserted across the inside of the tube, formed a horizontal support for the cellulose strip. The developing solvent, contained in a cylindrical dish at one end of the glass tube, was led onto the cellulose strip by means of an adsorbent cotton bridge. This apparatus can also be used for carrying out horizontal partition chromatographic analysis with the usual Whatman No. 1 papers. Methylated sugars show the same  $R_f$  value as those determined by either the ascending or descending techniques.

The thick cellulose sheets have been found to have a high loading capacity, *e.g.*, D-xylose in concentrations of 20 mg./cm. moved as a discrete band.

 TABLE I  
 SEPARATION OF SUGARS IN CELLULOSE SHEETS<sup>a</sup>

No.	Sugars	Solvent	Distance moved by solvent front (cm.)	Width of sugar bands (cm.)	$R_f$ values	
					Cellulose sheet	Whatman No. 1 paper
1	D-Glucose (15 mg.)	Phenol-water	26.0	4.1	0.40	0.38
	L-Rhamnose (17 mg.)				.64	.63
2 <sup>b</sup>	2,3-Dimethyl-D-glucose (14.2 mg.)	Methyl ethyl ketone-water azeotrope	34.5	5.5	.28	.28
	2,3,4,6-Tetramethyl-D-glucose (8.6 mg.)				.94	.82
3 <sup>c</sup>	L-Arabinose (2 mg.)	1-Butanol-ethanol-water	24.8	4.1	.27	.14
4	D-Xylose (100 mg.)	1-Butanol-ethanol-water	26.5	4.3	.24	.15
5 <sup>c</sup>	D-Glucose (2 mg.)	1-Butanol-ethanol-water	24.8	4.0	.20	.09
6	D-Glucose (14 mg.)	1-Butanol-ethanol-water	.. <sup>d</sup>	4.5	1.00 <sup>d</sup>	..
	L-Rhamnose (14 mg.)				1.63 <sup>d</sup>	..

<sup>a</sup> A cellulose strip 5 cm. in width was used in each experiment. <sup>b</sup> The methylated sugars could not be detected by the usual spray reagents (ammoniacal silver nitrate, *p*-aminodimethylaniline) due to the fact that aqueous solutions wash enough of the sugars into the inside of the sheet to make the level of sugar on the surface too low for detection by these reagents. They were detected, however, by spraying with a 3% solution of ethylleucine hydrochloride in 1-butanol and heating to 130° for about 10 minutes. The sugar bands fluoresced yellow in ultraviolet light. <sup>c</sup> These experiments were carried out in order to determine the  $R_f$  values of these sugars on the thick cellulose sheets. Each sugar was put onto the cellulose strip in the form of a spot. <sup>d</sup> The solvent was induced to flow off the end of the paper and the  $R_f$  value is quoted in reference to the movement of the glucose.

(1) Paper No. 2849, Scientific Journal Series, Minnesota Agricultural Experiment Station.

(2) A report of work done partially under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Northern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry.

(3) L. Hough, J. K. N. Jones and W. H. Wadman, *J. Chem. Soc.*, 2511 (1949).

(4) H. K. Mitchell and F. A. Haskins, *Science*, **110**, 278 (1949).

(5) H. K. Mitchell, H. Gordon and F. A. Haskins, *J. Biol. Chem.*, **180**, 1071 (1949).

(6) W. L. Porter, *Anal. Chem.*, **23**, 412 (1951).

(7) L. Zechmeister and L. Cholnoky, "Principles and Practice of Chromatography," John Wiley and Sons, Inc., New York, N. Y., 1941.

Moreover, successful separations of D-glucose and L-rhamnose, D-glucose and D-fructose, and 2,3-dimethyl- and 2,3:4,6-tetramethyl-D-glucose have been made using phenol-water, 1-butanol-ethanol-water and methyl ethyl ketone-water azeotrope, respectively. By lap-jointing two or three strips to

(8) P. C. Zamecnik, R. B. Loftfield, Mary L. Stephenson and Jean M. Steele, *Cancer Research*, **11**, 592 (1951).

(9) G. Yanofsky, E. Wasserman and D. M. Bonner, *Science*, **111**, 61 (1950).

(10) J. H. Mueller, *ibid.*, **113**, 405 (1950).

(11) The cellulose sheets from which Whatman ashless filter tablets are cut, were kindly furnished by H. Reeve Angel and Co., Inc.

gether it was possible to induce the solvent to flow two or three times the length of the first strip. It was somewhat surprising to find that the  $R_f$  values of sugars using 1-butanol-ethanol-water were higher with thick sheets than those obtained using Whatman No. 1 paper. The reason for this is not apparent.

Some examples of the application of the above technique are given in Table I.

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### Triesters of Carboxymethylmercaptosuccinic Acid<sup>1</sup>

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A number of esters of carboxymethylmercaptosuccinic acid have been described by Mulvaney, *et al.*<sup>2</sup> As part of a study on antioxidants, it was of interest to prepare several new trialkyl esters of this acid. These compounds and their physical properties are listed in Table I.

cleavage of the thioether linkages. In this manner, the sulfur could be determined quantitatively as sulfate. It is quite possible that the sulfones or the intermediate sulfoxides are formed but are unstable and react further.

#### Experimental

**Preparation of Triesters of Carboxymethylmercaptosuccinic Acid.**—The method used was similar to that described by Mulvaney,<sup>2</sup> except that sodium bisulfate was used as the catalyst, and is illustrated for the preparation of the triisobutyl ester. In a 300-ml. round-bottom flask fitted with a modified Dean and Stark apparatus used as a phase separator and to which was attached a reflux condenser, was placed 62.5 g. (0.3 mole) of carboxymethylmercaptosuccinic acid (Evans Chemetics, Inc.), 74 g. (1.0 mole) of isobutyl alcohol, 0.5 g. of sodium bisulfate and 50 ml. of benzene as a water entrainer. The mixture was heated under reflux for five hours, after which time the theoretical amount of water (16.4 ml.) had been collected. The reaction mixture was washed with three 50-ml. portions of a 10% sodium carbonate solution, then with water, and dried over anhydrous magnesium sulfate. The mixture was distilled and gave 90 g. (79.8%) of the triester, b.p. 167–169° (0.37 mm.). The other triesters, shown in Table I, were obtained in comparable yields.

**Reaction of the Tri-*n*-butyl Ester with Hydrogen Peroxide in Acetic Acid.**—In a 200-ml. round-bottom flask, fitted

TABLE I

R	<i>t</i> , °C.	B.P. <sup>3</sup>	Mm.	$n_D^{25}$	$d_4^{25}$	Calcd.	MR		Sulfur analyses, %	
							Found	Calcd.	Found	Found
Isobutyl	167–169	0.37	1.4583	1.042	98.0	98.6	8.54	8.65		
<i>n</i> -Hexyl	200–203	.40	1.4644	1.013	125.7	125.6	6.96	7.32		
2-Ethyl butyl	205–208	.40	1.4649	1.012	125.7	125.8	6.96	7.15		
2-Ethyl hexyl	222–227	.37	1.4663	0.9801	153.4	153.6	5.88	5.92		

Though somewhat unstable thermally, the esters may be distilled at the reduced pressures without appreciable decomposition. All of the esters are slowly hydrolyzed at room temperature by 5% aqueous potassium hydroxide. The tris-1,1-dihydroperfluorobutyl ester reacts rapidly with dilute potassium carbonate.<sup>4</sup> Esters of this fluoro alcohol which do not contain sulfur show no detectable hydrolysis under these conditions.<sup>5</sup>

Attempts to oxidize the triesters to sulfoxides or sulfones with chromic acid or potassium permanganate were unsuccessful. Hydrogen peroxide in acetic acid reacted with the tri-*n*-butyl ester,<sup>6</sup> but only a high yield of *n*-butyl acetate and a sulfur-containing residue, which may have been the original mercapto acid, were isolated. The formation of *n*-butyl acetate could result from oxidation or hydrolysis of the ester groups followed by esterification of the alcohol thus obtained by the acetic acid. Drastic oxidation with nitric or perchloric acids resulted in

with a reflux condenser, was placed 22.6 g. (0.2 mole based on 100% H<sub>2</sub>O<sub>2</sub>) of 30% hydrogen peroxide and 50 ml. of glacial acetic acid. The mixture was heated with a Glas-Col mantle at 85° for one hour. The mixture was cooled to 25° and then 37.6 g. (0.1 mole) of the tri-*n*-butyl ester was added. The mixture was heated under reflux for two days. The upper, water-insoluble layer was separated and the lower acid layer was neutralized with a dilute solution of sodium bicarbonate and extracted with ether. The ether layer was combined with the original water-insoluble layer and dried over anhydrous sodium sulfate. The ether was removed by distillation and there was obtained 28.0 g. (80.5%) of *n*-butyl acetate, b.p. 121–124° and about 5 g. of a sulfur-containing residue, which decomposed on heating. This may have been carboxymethylmercaptosuccinic acid.

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### Preparation and Properties of Pentamethyleneketene Monomer and Dimer

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Recent studies<sup>1,2</sup> of mono- and disubstituted ketenes suggested investigation of the dehydrohalogenation products of hexahydrobenzoyl chloride.

(1) Opinions expressed are those of the authors and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

(2) J. F. Mulvaney, J. G. Murphy and R. L. Evans, *THIS JOURNAL*, **70**, 2428 (1948).

(3) Boiling points uncorrected.

(4) M. Hauptschein, private communication.

(5) R. Filler, J. V. Fenner, C. S. Stokes, J. F. O'Brien and M. Hauptschein, *THIS JOURNAL*, **75**, 2693 (1953).

(6) Hardesty Chemical Co., Inc., New York City.

(1) C. M. Hill, H. I. Schofield, A. S. Spriggs and M. E. Hill, *THIS JOURNAL*, **73**, 1660 (1951).

(2) C. M. Hill and G. W. Senter, *ibid.*, **71**, 364 (1949).