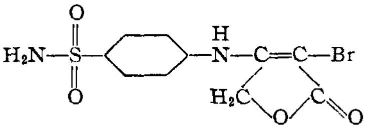
The bromine observed was 24.11 and 23.86, in good agreement with the theoretical value of 24.00 for the compound formed by splitting out water.

The two possibilities are then N^4-α-bromotetronyl sulfanilamide and N^1-α-bromotetronyl sulfanilamide. The N^1-compound would be analogous to a secondary sulfonamide since α-bromotetronic acid is a strong acid *pKa* 2.23,[2] and such a sulfonamide would be sufficiently acidic to titrate accurately to the phenolphthalein end-point. On the other hand, the N^4-compound would have very weak acidic properties. Our compound has very weak acidic properties and gives a very high equivalent weight at the phenolphthalein end-point.

The N^1-compound would likewise be expected to undergo diazotization at 0°, couple and give a bright color with alkaline α-naphthol, while the N^4-compound would not give a color. Our compound gives no color other than a pale yellow, which was also obtained with a blank. The compound can, however, be hydrolyzed in either 10% hydrochloric acid or 10% sodium hydroxide to give a compound that gives the test for a primary aromatic amine group.

An attempt was made to condense α-bromotetronic acid with a compound in which the amino group in sulfanilamide was blocked, N^4-acetylsulfanilamide. The same conditions were used that gave the best results with sulfanilamide but no evidence of any reaction was obtained and 90% of the N^4-acetylsulfanilamide was recovered unchanged.

The evidence from all sources indicates that the compound is N^4-α-bromotetronyl sulfanilamide.



This compound is of interest because it is a new type of sulfanilamide derivative formed by condensing an enol with sulfanilamide. The compound has a possible tautomeric form but the structure given is the more likely one due to the stability resulting from the resonance forms that are possible with it but not with its tautomer.

Preliminary investigation of the pharmacology of the compound in Dr. Chauncey D. Leake's laboratory in the University of California Medical School indicates that the compound has a very low toxicity. Twelve grams per kilo of body weight were given orally to mice without any fatalities. The compound has a protective action against β-hemolytic streptococcus that is about equal to that of sulfanilamide.

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[2] Kumler, THIS JOURNAL, **60**, 859 (1938).

The Quantitative Analysis of Mixtures of Polyoxyethylene Glycols by Fractional Distillation[1]

BY STANLEY PERRY AND HAROLD HIBBERT

A method for the quantitative separation of the products of hydrolysis of methylated polysaccharides by fractional distillation has been used with some success by Haworth and co-workers[2] in molecular weight determinations by the end-group method. More recently, Hess[3] has modified the method so as to make it even more sensitive for the determination of tetramethyl methyl glucoside. However, the efficacy of a distillation analysis of this type is not very generally recognized, so that it is of some interest that a similar accurate separation has now been found possible with complex mixtures of polyoxyethylene glycols, $HOH_2C(CH_2OCH_2)_nCH_2OH$. Thus, the quantitative separation of these liquid polymers has been obtained by subjecting synthetic mixtures to fractional distillation, the course of the separation being followed in each case by the change in refractive index of the distillate.

The applicability of the process to the separation of unknown mixtures was fully established by collaborative experimentation, the senior author preparing synthetic mixtures which were then separated into their components by the junior author, who was not informed of the number or proportions. Under these conditions, it was not only possible to detect which members were present and which were not, but also to isolate and determine quantitatively the proportion of each with an accuracy of 96 to 99.8%. This is illustrated in the accompanying tables of data.

The mixtures used in these experiments were prepared from carefully purified products pre-

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[1] Part LX of the series "Studies on Reactions Relating to Carbohydrates and Polysaccharides."

[2] Haworth and Machemer, *J. Chem. Soc.*, 2270 (1932); Haworth and Percival, *ibid.*, 2277 (1932).

[3] Hess and Neumann, *Ber.*, **70B**, 710 (1937).

viously synthesized by methods which have been described elsewhere.[4]

TABLE I

DISTILLATION ANALYSIS OF A MIXTURE OF POLYOXYETHYLENE GLYCOLS

Type of glycol	Taken, g.	Found, %	Actual, %	n^{20}_D pure glycol
Ethylene	6.16	29.5	29.5	1.4324
Dioxyethylene	None	0	Absent	1.4477
Trioxyethylene	4.34	20.8	20.8	1.4568
Tetraoxyethylene	6.00	28.8	29.9	1.4604
Pentaoxyethylene	None	0	Absent	1.4629
Hexaoxyethylene	4.35	20.85	19.9	1.4647

TABLE II

DETAILS OF THE ANALYSIS[a]

Fraction	Found, g.	n^{20}_D	Distn. temp., °C.	Glycol
1	5.87	1.4324–1.4325	46– 48	Ethylene
2	0.21	1.3425–1.4332	48– 49	
3	.34	1.4330–1.4564	97– 98	
4	3.91	1.4564–1.4568	99–104	Trioxyethylene
5	0.46	1.4568–1.4599	106–108	
6	5.43	1.4599–1.4605	125–144	Tetraoxyethylene
7	0.37	1.4605–1.4622	147–165	
8	.25	1.4622–1.4642	162	
9	3.52	1.4642–1.4646	163–167	Hexaoxyethylene
10	0.50	....	Residue	

[a] Total weight, 20.85 g.; pressure, 0.001–0.002 mm.

The distillations were carried out in small flasks equipped with a form of Widmer column,[5] *i. e.*, a vacuum-jacketed vertical tube with circular indentations (one ring for every 7 mm. length) of outside diameter 1 cm. The inside diameter of the outside tube was about 14 mm. A very slow rate of distillation was used, but otherwise only the ordinary precautions for fractionating under reduced pressure were applied.

(4) Perry and Hibbert, *Can. J. Research*, **14B**, 77 (1936).

(5) Widmer, *Helv. Chim. Acta*, **7**, 59 (1924).

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The Mutarotation of *d*-Glucose in Absolute Methanol

BY H. H. ROWLEY AND S. DAVID BAILEY

Numerous investigators have studied the mutarotation of *d*-glucose in an effort to determine the number as well as the amount of isomers present in a solution of *d*-glucose. Some[1,2,3] draw conclusions from their work that more than two forms of glucose are present in solution. If the mutarotation of glucose involves only two isomers, the observed reaction rate should be that for two opposing reactions and the kinetic data should fit a first-order equation. The presence of a third form in concentrations comparable to the other two forms would cause the reaction to deviate considerably from the first order. For aqueous solutions the mutarotation of *d*-glucose appears to follow a first-order reaction exactly as observed by many investigators.[4,5,6]

Since methanol acts less readily than water as a catalyzer for the reaction, it is logical to assume that the mutarotation in this solvent would be much slower than in water. If this is the case and the same mechanism is operative in methanol as in water, any divergence from a first-order process would be more easily observed. Worley and Andrews[2] claimed that one run in methanol with α-*d*-glucose showed a lag for over an hour at 25°. However, no data were given to support this claim. Aside from their work, little has been reported on methanol solutions and, since previous investigations are not too consistent, it was decided to study the mutarotation of *d*-glucose in absolute methanol at 25, 35 and 45°.

Discussion of Results

Anhydrous α- and β-*d*-glucose were obtained through the courtesy of the Corn Products Refining Co. of Argo, Ill. The alpha sugar was further purified by the method of Hudson and Yanovsky[7] while the beta sugar was treated by the method of Hudson and Dale.[5] The physical constants of the purified sugars agreed with accepted literature values. The absolute methanol was a synthetic product further dried with metallic sodium and fractionally distilled. The concentration of the solutions ranged from 0.6 to 1.3 g. of sugar per 100 ml. of solution. The course of the mutarotation was followed polarimetrically in jacketed tubes using a sodium arc as a source of illumination.

The velocity constants $(k_1 + k_2)$ for the reaction were calculated from Hudson's[8] equation which is based on the assumption that there is a simple equilibrium between the alpha and beta isomers of *d*-glucose. Of the numerous runs made,

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(1) Riiber and Minsaas, *Ber.*, **59**, 2266 (1926).

(2) Worley and Andrews, *J. Phys. Chem.*, **31**, 742, 882, 1880 (1927); **32**, 307 (1928).

(3) Hendrick and Steinbach, *ibid.*, **42**, 335 (1938).

(4) Isbell and Pigman, *J. Research Natl. Bur. Standards*, **18**, 141 (1937).

(5) Hudson and Dale, THIS JOUNAL, **39**, 320 (1917).

(6) Nelson and Beegle, *ibid.*, **41**, 559 (1919).

(7) Hudson and Yanovsky, *ibid.*, **39**, 1015 (1917).

(8) Hudson, *ibid.*, **26**, 1065 (1904).