The relationship between the number of maxima in the turbidity curves and the number of demonstrable components in the system is not direct. Turbidity does not develop if all components in the system are soluble under the conditions of the experiment and no interaction to produce insoluble products occurs. Where turbidity does occur, if the turbidity is simply insolubility without interaction, one peak apparently develops for each insoluble component. The *p*H at which the maximum occurs is presumably related to the isoelectric point of the component. When an interaction between two or more components does occur, the result may be the formation of an insoluble complex. The maximum with respect to *p*H is then indicative of the *p*H of interaction. Conversely, an interaction to alter the solubility of an otherwise insoluble component likewise may occur. As can be seen in Fig. 2 component 6.2P by itself or mixed with 6.2S gives a maximum at *p*H 6.2 in the turbidity curve. The maximum at *p*H 6.2 is not present in starting fraction 5.1P, suggesting that one or both of the two components in 3.0P interacts with 6.2P and that the reaction product is soluble at *p*H 6.2.

We have found turbidity analyses helpful in suggesting *p*H and ionic strength conditions at which separations may be expected to occur. Our experience with the method is too limited, however, to generalize the relationship. The purpose of this communication is merely to direct attention to the method and to indicate that a relationship exists.

It seems likely that turbidity analysis can be adapted to the study of a variety of protein interactions. Under proper conditions the method is useful as an additional, and possibly fairly sensitive, criterion of purity. A simple turbidity curve or failure to obtain turbidity provides no information about purity; a complex turbidity curve, however, almost certainly indicates heterogeneity.

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A Twenty-six-membered Cyclic Dimercaptal[1]

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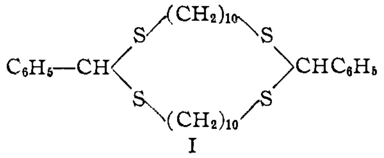
In a study of the acid-catalyzed reaction of decamethylenedithiol and benzaldehyde in dioxane solutions at 30°, a crystalline solid separated from solution in every experiment to the extent of about 50% of the weight yield. When this solid was isolated by filtration and the solvent evaporated, the expected polymercaptal[2] was obtained. The solid material after repeated recrystallizations from benzene and chloroform melted sharply. Analyses and molecular weight determinations indicated that it was the 26-membered cyclic dimercaptal (I) similar in structure to the 16- and 18-membered ring cyclic mercaptals which were reported by Autenrieth and Beutell from *p*-xylyl dimercaptan and aryl aldehydes and from *m*-xylyl dimercaptan and acetone.[3]



I

Further evidence for the cyclic structure was furnished from the infrared absorption of the mercaptal since this showed no hydroxyl absorption bands, no carbonyl bands and no mercaptan bands. The X-ray pattern indicated definite crystallinity.[4]

Oxidation of the cyclic mercaptal with monoperphthalic acid in ether solution converted it in good yield to the tetrasulfone which melted at 195–196°.

The ease of formation and good yield of this ring containing 26 members is somewhat unexpected. Other examples of this type of cyclic molecule are being sought.

Experimental

2,15-Diphenyl-1,3,14,16-tetrathiacyclohexacosane.—A solution of 12.9 g. (0.0626 mole) of freshly distilled decamethylenedithiol in 125 ml. of dioxane[5] was added to a solution of 6.6 g. (0.0623 mole) of purified[6] benzaldehyde in 125 ml. of dioxane. A solution of 25 ml. of dioxane saturated with dry hydrogen chloride at room temperature was then added to the mixture. The system was flushed with nitrogen, stoppered, and stirred for four days at room temperature (30–35°). The solid material was removed by filtration and dried to give 9 g. (50%) of white material which melted at 125–128°. After recrystallization from benzene, it weighed 5.7 g. and melted at 133–134°.

Repeated recrystallization from benzene, chloroform (three times) and then benzene again gave a sample of m.p. 135.5–135.8°.

Anal.[7] Calcd. for $C_{34}H_{52}S_4$: C, 69.33; H, 8.90; S, 21.77. Found: C, 70.01; H, 9.07; S, 21.20.

The molecular weight determination on this material was carried out by the method of Menzies and Wright.[8] The ebullioscopic solvent (28 ml.) was thiophene-free reagent-grade benzene which was redistilled and fractionally crys-

TABLE I

EBULLIOSCOPIC MOLECULAR WEIGHT DETERMINATIONS OF BENZALDEHYDE–DECAMETHYLENEDITHIOL CONDENSATION PRODUCT

Expt. no.	*w*, g.	Δ,[a] mm.	Δ*p*,[b] mm.	Δ*t*,[c] °C.	*M*
0	0	8.3(Δ_0)	0	0	...
1	0.0737	11.1	2.8	0.01414	600
2	.1258	13.1	4.8	.02424	596
3	.1884	15.9	7.6	.03838	566
4	.2464	18.1	9.8	.04949	574
				Average	584

[a] The observed differential reading on the Menzies–Wright water thermometer; the first of these is the Δ_0 value. [b] $\Delta p = \Delta - \Delta_0$. [c] $\Delta t = 0.00505\Delta p$.

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(1) The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

(2) C. S. Marvel, Elizabeth H. H. Shen and R. R. Chambers, THIS JOURNAL, **72**, 2106 (1950).

(3) W. Autenrieth and F. Beutell, *Ber.*, **42**, 4346, 4357 (1909).

(4) We are indebted to Dr. R. L. Bohon of the Anderson Physical Laboratory, Champaign, Ill., for the infrared data and to Mr. W. E. Thatcher of this Laboratory for the X-ray examination.

(5) Recently purified by the method of L. F. Fieser, "Experiments in Organic Chemistry," Part II, Second Edition, D. C. Heath and Co., Boston, Mass., 1941, p. 369.

(6) By washing with aqueous sodium carbonate, drying, and twice redistilling under nitrogen.

(7) Microanalyses by C. W. Beazley, Micro-Tech Laboratories, Skokie, Ill.

(8) A. W. C. Menzies and S. L. Wright, Jr., THIS JOURNAL, **43**, 2315 (1921).

tallized. The results of those determinations are recorded in Table I.

2,15-Diphenyl-1,3,14,16-tetrathiacyclohexacosane Tetrasulfone.—The cyclic dimercaptal was oxidized to the corresponding tetrasulfone by the method of Drew.[9] A mixture of 2.90 g. (0.0049 mole) of the cyclic mercaptal and 350 ml. of a 0.14 *M* solution (0.049 mole) of monoperphthalic acid[9,10] in dry ethyl ether was placed in an erlenmeyer flask fitted with a magnetic stirrer and a soda-lime tube, and stirred for 24 hours at room temperature. Additional dry ether (200 ml.) and 100 ml. of the monoperphthalic acid solution were added and the mixture was stirred for 24 hours. A final 250-ml. portion of the monoperphthalic acid solution was added and the mixture was stirred for still another 48 hours.

The product was collected on a filter, affording 3.36 g. (95%) of white solid, m.p. 189–191°. After several recrystallizations from chloroform, the analytical sample had m.p. 195–196°.

Anal. Calcd. for $C_{34}H_{52}S_4O_8$: C, 56.95; H, 7.31; S, 17.89. Found: C, 57.46; H, 7.39; S, 18.32.

The same tetrasulfone was obtained in lower yield by an acid permanganate oxidation of the cyclic mercaptal.

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[9] H. F. Drew, Ph.D. Thesis, University of Minnesota, Minneapolis, Minn., November, 1951, p. 52.

[10] H. Böhme, *Org. Syntheses*, **20**, 70 (1940).

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2,5-Dimethyl-D-glucofuranose and Two New Crystalline Derivatives

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In connection with studies on the flameproofing of cotton fiber by reaction with titanium compounds it was desired to investigate, separately, the reactivity of the various glucoside hydroxyl pairs with titanium. This was accomplished by the use of model glucosides having all but two positions blocked by substituent groups. One of the model glucosides employed for this purpose was methyl 2,5-dimethyl-α-D-glucofuranoside, which has not previously been described in the literature. Its preparation and properties are described in this note. Its reactivity with organic titanates will be considered in a separate communication together with the reactivity of cellulose and several other model glucosides.

In a review article published in 1950, Bourne and Peat[1] were able to list all but three of the twenty-three possible methyl ethers of D-glucofuranose and D-glucopyranose as having been prepared in pure form or in the form of a closely related derivative. One of the three glucose ethers which had not been reported at that time was 2,5-dimethyl-D-glucofuranose, whose only known derivatives were in the distantly related glucuronic acid and 3,6-anhydroglucose series. This report records the preparation of two crystalline derivatives of 2,5-dimethyl-D-glucofuranose: namely, methyl 2,5-dimethyl-α-D-glucofuranoside and its 3,6-diacetate. From either of these derivatives the parent dimethyl glucose ether may be obtained in solution upon hydrolysis. Attempts to isolate the reducing sugar in crystalline condition have so far been unsuccessful, apparently because it undergoes self-condensation when water is evaporated from its aqueous solutions.

The structures of the new derivatives are established only by their method of synthesis, the reduction of methyl 2,5-dimethyl-α-D-glucurone with lithium aluminum hydride. They have not been directly related with any other known glucose derivatives. However, since the reduction would not be expected to alter the configuration at any of the asymmetric centers, assignment to the glucose series can be made with considerable assurance.

Experimental

Methyl 2,5-Dimethyl-α-D-glucofuranoside.—Three grams of lithium aluminum hydride was suspended in 100 ml. of dry ether in a flask attached to an extraction apparatus. A quantity of 2.13 g. of methyl 2,5-dimethyl-α-D-glucurone[2,3] was placed in a sintered glass thimble which was located in the extraction apparatus so that the ether upon refluxing slowly transferred the glucurone to the slurry of reducing agent. After refluxing for six hours and standing at room temperature overnight the excess lithium aluminum hydride was destroyed with 300 ml. of moist ether. Filtration and extraction of the precipitated hydroxides yielded an ether solution of the product which upon concentration deposited 1.44 g. of crystals. Recrystallization from ether gave a product melting between 55° and 72°. At 0.001 mm. it distilled at about 70° (bath) and the distillate crystallized readily on the condenser. In most cases the distillate melted sharply at 55–57°, but in some experiments a higher melting form, m.p. 70–72°, was encountered. The higher melting form could also be obtained by recrystallization from ether, but it gradually changed to the lower melting form on standing. Both forms displayed the same specific rotations (sodium D line, 25°) which were as follows: in methanol, +140° (*c* 1.0); in ether, +157° (*c* 1.0); in water, +124° (*c* 0.87).

Anal. Calcd. for $C_9H_{18}O_6$ (222.23): C, 48.64; H, 8.16; OCH_3, 41.89. Found: C, 48.59, 48.30; H, 8.27, 8.14; OCH_3, 41.35, 41.39.

The glucoside did not contain any saponifiable ester or lactone.

Methyl 2,5-Dimethyl-3,6-diacetyl-α-D-glucofuranoside.—A quantity of the above methyl glucoside weighing 1.19 g. was dissolved in 4 ml. of pyridine and treated with 2 ml. of acetic anhydride. The solution was warmed to 80° for two hours, then evaporated to dryness in vacuum. The sirupy residue crystallized from a mixture of ether and petroleum pentane; yield 0.64 g. After recrystallization from the same solvent this material had a very sharp melting point of 46–47°. Its specific rotation in chloroform was +95° (*c* 2.6), and in ether, +133° (*c* 3.6).

Anal. Calcd. for $C_{13}H_{22}O_8$ (306.31): C, 50.97; H, 7.24; CH_3CO, 28.1. Found: C, 50.91, 51.05; H, 7.24, 7.23; CH_3CO (by saponification and back titration), 28.5, 28.4.

Deacetylation of this substance with a trace of sodium methoxide in methanol yielded the original glucoside. m.p. 55–56°; sp. rot. in ether, +158°.

2,5-Dimethyl-D-glucofuranose by Hydrolysis of Its Glucoside. (a) With Hydrochloric Acid.—Twenty-six mg. of the glucoside, dissolved in 2.4 *N* hydrochloric acid, changed in 90 minutes at room temperature from strongly dextrorotatory to zero rotation. In another experiment 300 mg. of the glucoside in *N* hydrochloric acid reached a constant zero rotation on standing overnight at room temperature. The chloride ion was removed on a small column of Amberlite 400[4] resin and the solution evaporated to dryness. The residue of 163 mg. of a colorless sirup failed to crystallize on standing.

(b) With Amberlite 120H.[4]—In this experiment 628 mg. of the crystalline glucoside was dissolved in 25 ml. of water and treated with 1 g. of moist Amberlite 120H resin which previously had been boiled with several changes of distilled water. Upon refluxing, the rotation of the solution changed

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[1] E. J. Bourne and S. Peat, *Advances in Carbohydrate Chemistry*, **5**, 145 (1950).

[2] J. Pryde and R. T. Williams, *Biochem. J.*, **27**, 1205 (1933).

[3] R. E. Reeves, THIS JOURNAL, **62**, 1616 (1940).

[4] The mention of a trade product does not imply its endorsement by the Department of Agriculture over similar products not named.