6-benzoate. Benzoylation of 45 mg. of the substance was effected as described for the rebenzoylation of dibenzylideneglucose diethyl mercaptal and the product was crystallized from ethanol; yield 39 mg.; m. p. 159–160° (mixed m. p. unchanged).

We wish to acknowledge the valuable assistance rendered by Messrs. J. F. Shea (W. P. A.; Project No. 13612) and D. M. Miller (N. Y. A.).

Summary

1. The reaction between *d*-glucose diethyl mercaptal 6-benzoate (I) and benzaldehyde–zinc chloride has been shown to vary in speed with the sample of zinc chloride used but always to consist of the rapid formation of dibenzylidene-*d*-glucose diethyl mercaptal 6-benzoate (II), followed by the relatively slow formation of the non-reducing dibenzylidene-*d*-glucose 6-benzoate (III) of Papadakis.

2. The demonstrated formation of III from II and from dibenzylidene-*aldehydo*-*d*-glucose 6-benzoate (V) makes probable the consecutive changes I ⟶ II ⟶ V ⟶ III.

3. Removal of the benzylidene groups from II produces I.

4. Rebenzoylation of the non-reducing dibenzylidene-*d*-glucose (IV) of Papadakis yields III.

5. Demercaptalation of II gives V, which forms a thiosemicarbazone and is isomeric with III.

6. Debenzoylation of II produces (2,3,4,5)-dibenzylidene-*d*-glucose diethyl mercaptal (VII), which forms II on rebenzoylation.

7. Demercaptalation of VII yields an amorphous, reducing (2,3,4,5)-dibenzylidene-*d*-glucose (VIII), characterized by its thiosemicarbazone (IX).

8. With the exception of VIII, all compounds herein reported have been obtained in crystalline condition and their constants determined.

COLUMBUS, OHIO RECEIVED JUNE 11, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

The Chemistry of Naturally Occurring Monohydrohexitols[1]

BY WERNER FREUDENBERG AND E. F. ROGERS

In the course of some studies on the structure and configuration of synthetic anhydrohexitols, a literature search covering occurrence, properties and structure of natural monoanhydrohexitols was essential for comparison. The results are summarized in Table I.

Both on oxidation with sodium hypobromite yield products which give the same 1,5-anhydrofructosazone,[9,3,10] while hydrogen peroxide forms hexoses identified as glucosazone. Hence, styracitol and polygalitol have identical ring structure and are epimeric. The synthesis of the former, as carried out by Zervas,[11] involved hydrogenation of 2-oxyglucal acetate (I) and subsequent deacetylation of the reduced acetyl product. The conclusion, therefore, that the synthetic product was 1,5-anhydrosorbitol (II) found general acceptance. As a consequence polygalitol was given

TABLE I

NATURAL ANHYDROHEXITOLS, $C_6H_{12}O_5$, REPORTED IN LITERATURE

Name	Author	Source	Free alcohol		Acetyl der.,	Dibenzal der.	
			M. p., °C.	Sp. rot.	M. p., °C.	M. p., °C.	Sp. rot.
Styracitol	Asahina[2]	*Styrax obassia*	155	−49°	66	163–165	−148.7°
						192–193	− 80.5°
	Shinoda[3]	*Polyg. ten.*					
Polygalitol	Chodat[4]	*P. amara*	143	+43°	73–75	...	...
	Piccard[5]	*P. vulgaris*					
Aceritol	Perkin[6]	*Acer ginnala*	142	+39°	74–75	...	...
Viburnitol	Hérissey and Poirot[7]	*Viburnum tinus*	180–181	−49°	...	...	...
Anhydromannitan	Haas and Hill[8]	*Pelvetia can.*	...	...	...	165–168	...

Of these compounds structural formulas have only been assigned to styracitol and polygalitol.

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(1) Reported before the Organic Division, A. C. S. Meeting, Chapel Hill, N. C., April, 1937.

(2) Asahina and Takimoto, *Ber.*, **64**, 1803 (1931).

(3) Shinoda, Sato and Sato, *ibid.*, **65**, 1219 (1932).

(4) Chodat, *Arch. sci. phys. nat.*, [3] **20**, 599 (1888).

(5) Piccard, *Bull. soc. chim. biol.*, **9**, 692 (1927).

(6) Perkin and Uyeda, *J. Chem. Soc.*, **121**, 66 (1922).

(7) Hérissey and Poirot, *Compt. rend.*, **203**, 148 (1936).

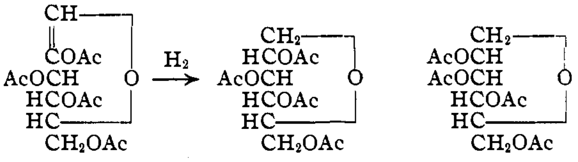
(8) Haas and Hill, *Biochem. J.*, **23**, 1000 (1929).

(9) Asahina, *Ber.*, **45**, 2365 (1912).

(10) Bergmann and Zervas, *ibid.*, **64**, 1436, 2032 (1931).

(11) Zervas, *ibid.*, **63**, 1689 (1930).

the structure of a 1,5-anhydromannitol[3] (III).



I II III

Some doubt still remains as to the configuration on carbon number two which in the course of the synthesis has become asymmetrical.[12]

A study of the rate of lead tetraacetate oxidation was chosen to differentiate between the two possible configurations (II) and (III). 1,5-Anhydromannitol (III) has one *cis*-glycol grouping; 1,5-anhydrosorbitol (II) has none. Criegee[13] has shown that *cis*-glycols are cleaved considerably faster than the *trans*-form. The rate of oxidation of polygalitol and styracitol under identical experimental conditions should therefore indicate which is anhydromannitol. Table III in the experimental part shows the results of three duplicate titrations.

Since styracitol is oxidized approximately twice as rapidly it appears to be anhydromannitol and polygalitol must have the configuration originally assigned to styracitol.

The following consideration leads to the same conclusion: as a general rule, of glucose and mannose derivatives with identical ring structures, the former have higher dextro rotation than the latter. Applied to our problem the higher rotation (+43°) is exhibited by polygalitol; hence it has the sorbitol structure while styracitol (−49°) is the corresponding mannitol anhydride. In addition Hudson's rule of optical superposition supports our view.

The theoretical relationship of the semi-acetal or glycoside of either mannose or glucose to the 1,5-anhydrohexitols is evident as substitution of hydrogen for hydroxyl or methoxyl gives either styracitol or polygalitol, carbon atom number one thus becoming symmetrical. The differences between the molecular rotations of α-*d*-mannose and α-*d*-glucose or between α-methylmannoside and α-methylglucoside (*assuming that α-mannose has a trans configuration of the hydroxyls on carbon one and two*), should equal the difference in molecular rotations of styracitol and polygalitol. This last difference (equation 5) falls almost exactly between the other two (equations 3 and 4). Obviously the differences in molecular rotations, assuming reversed configuration (equation 6), gives a positive value which seems impossible to interpret.

TABLE II

MOLECULAR ROTATIONS OF STYRACITOL AND POLYGALITOL IN COMPARISON TO MANNOSE, GLUCOSE, α-METHYLGLUCOSIDE AND α-METHYLMANNOSIDE

α-*d*-Mannose = A − B α-*d*-Glucose = A + B

M_D mannose − M_D glucose = A − B − A − B = −2B (1)
M_D mann. anh. − M_D sorb. anh. = −B − B = −2B (2)
M_D mannose − M_D glucose = 5400 − 19800 = −14400 (3)
M_D-oside − M_D-oside = 15248 − 30846 = −15598 (4)
M_D styrac. − M_D polyg. = −8101 − 7052 = −15153 (5)
M_D polyg. − M_D styrac. = +7052 + 8101 = +15153 (6)

The correctness of these conclusions is at present being tested by synthetic work in this Laboratory.

As to aceritol we found that this anhydrohexitol is identical with polygalitol. A sample, which was obtained through the courtesy of Professor Perkin, showed a slightly higher rotation (+43.8°) than the value reported by Perkin and Uyeda[6] (+39°). The melting points were identical and no depression was observed when a mixed melting point was taken.

Nothing definite can be stated in regard to the structure of the remaining anhydrohexitols in Table I.

A sample of dibenzal-mannitan, which was obtained from Professor Haas, could be shown not to be identical with dibenzalstyracitol. The latter is known in two modifications having specific rotations of −148.7 and −80.5°. Dibenzalmannitan in the same solvent, chloroform, rotates −29°. Our sample was not sufficient for hydrolysis of the benzal groups and identification of the parent anhydro alcohol.

Information in regard to viburnitol is still lacking; no derivatives have been described nor have hydroxyl determinations been made. For its structure, however, we have excluded the possibility of a 1,5-anhydrodulcitol. This has been obtained as a colorless, water soluble and only slightly levorotatory sirup, $[\alpha]^{23}\text{D}$ −7°, of unproved purity. For identification a tetraacetyl derivative has been prepared in crystalline form; m. p. 108°; $[\alpha]^{22}\text{D}$ −15.3° ($CHCl_3$). The synthesis performed was analogous to the styracitol preparation, the starting material being tetraacetyl-2-

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[12] Compare the analogous case of glucal and "mannal": Levene and Tipson, *J. Biol. Chem.*, **90**, 89 (1931); Gehrke and Obst, *Ber.*, **64**, 1724 (1931).

[13] Criegee, *Ann.*, **495**, 216 (1932); **507**, 159 (1933).

oxy-galactal[14] which was hydrogenated in the presence of palladium.

Experimental[15]

Styracitol.—This compound was prepared according to the method of Zervas[11] by catalytic hydrogenation of tetraacetyl-2-oxyglucal and deacetylation of the hydrogenated product. The observations of Zervas were confirmed. Recrystallization from methyl alcohol gave small rods, melting at 155°, $[\alpha]^{24}_D$ −48.25° (H_2O, $c = 1.5$), $[\alpha]^{23}_D$ −50.5° (3.5% $H_3BO_3 - H_2O$, $c = 2.0$).

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.89; H, 7.37. Found: C, 44.03; H, 7.82.

Polygalitol.—*Polygala senega* was found to be a satisfactory source of polygalitol. The method described by Shinoda[3] for isolation from *P. tenuifolia* was applied. Briefly, the pulverized drug (1 kg.) was extracted thoroughly with methyl alcohol, the extract concentrated, neutralized with magnesia and then dried in the air. On treatment of the dark brown gum so obtained with absolute methyl alcohol the magnesium salts remained undissolved. The large bulk of saponin present was next removed by careful addition of ether to the alcohol solution. The filtrate was then concentrated with removal of ether and, after several days of standing in the ice box, deposited 2.2 g. of crude polygalitol. Recrystallization from methyl alcohol gave small prisms, m. p. 142–143°, $[\alpha]^{19}_D$ +42.86° (H_2O, $c = 1.0$), $[\alpha]^{23}_D$ +45.0° (3.5% $H_3BO_3 -$ H_2O, $c = 1.0$).

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.89; H, 7.37. Found: C, 44.12, 43.96; H, 7.14, 7.16.

Comparison of Aceritol and Polygalitol.—Aceritol (Professor Perkin's sample) melted at 142–143°, $[\alpha]^{19}_D$ +43.8° (H_2O, $c = 1.0$). A mixture with polygalitol showed no depression in melting point.

TABLE III

OXIDATION OF STYRACITOL AND POLYGALITOL WITH LEAD TETRAACETATE

	Sample, mg.	0.018 *N* $Pb(OAc)_4$ Initial ml.	0.018 *N* $Pb(OAc)_4$ Reacted ml.	Time, hr.	$Pb(OAc)_4$ Reacted, %
Styracitol	50.0	40.0	26.9	15	67.3
Polygalitol	49.9	40.0	11.8	15	29.5
Styracitol	89.0	85.0	37.5	9	44.2
Polygalitol	89.2	85.0	17.4	9	20.5
Styracitol	70.0	107.0	31.2	9	29.2
Polygalitol	70.2	107.0	16.9	9	15.8

Lead Tetraacetate Oxidations. (*Table III*).—Approximately equal weights of polygalitol and styracitol were placed in dry flasks and dissolved in 5 ml. of C. P. glacial acetic acid. The titration blank of the solvent was negligible. Equal volumes of standardized lead tetraacetate solution were then added through a buret and the flasks tightly stoppered. After a set period the unreacted tetraacetate was decomposed by addition of 2 volumes of an aqueous solution containing 20 g. of potassium iodide and 500 g. of sodium acetate per liter. The buffered iodine solution formed was then titrated with standard thiosulfate, giving directly the amount of unreacted lead tetraacetate or indirectly the reacted tetraacetate.

Tetraacetyl Oxygalactal.—Tetraacetyl oxygalactal[14] suitable for hydrogenation is best obtained by recrystallization of the original crude product first from alcohol, then from water. The alcohol crystallized material still contains a substance which inhibits hydrogenation. By concentrating the mother liquors of the water crystallization a compound was isolated which appears to be 2,3,4,6-tetraacetyl-*β*-*d*-galactose.[16] It melts at 107° and exhibits mutarotation. Equilibrium was reached within approximately seventy-six hours $[\alpha]^{25}_D$ +77.0° (EtOH, $c = 4.0$).

Anal. Calcd. for $C_{14}H_{20}O_{10}$: C, 48.28; H, 5.79. Found: C, 48.51, 48.33; H, 5.78, 5.92.

Tetraacetyl-1,5-anhydrodulcitol (-talitol?).—Four grams of tetraacetyl oxygalactal, dissolved in 50 ml. of glacial acetic acid, was hydrogenated in the presence of 1 g. of palladium black. Hydrogen intake (1 mole) reached theoretical in one half hour. The filtered solution was evaporated to dryness *in vacuo* and the acid-free sirup crystallized from a small amount of methyl alcohol. After two recrystallizations from methyl alcohol, 2.8 g. of material was obtained as prisms, melting at 108°, $[\alpha]^{22}_D$ −15.31° ($CHCl_3$, $c = 2.0$).

Anal. Calcd. for $C_{14}H_{20}O_9$: C, 50.60; H, 6.07. Found: C, 50.79, 50.61; H, 6.15, 6.07.

1,5-Anhydrodulcitol (-talitol?).—Two grams of tetraacetyl-1,5-anhydrodulcitol was dissolved in alcohol and the solution, after mixture with a paste containing 5 g. of barium hydroxide in 70 ml. of water, was shaken mechanically for ten hours. The barium was removed quantitatively with sulfuric acid. After distillation of the solvent a colorless, water-soluble sirup was obtained which resisted all efforts to crystallize it. It was dried by repeated evaporation with absolute alcohol and its specific rotation determined without further purification, $[\alpha]^{23}_D$ −7.34° (H_2O, $c = 1.0$). An attempt to obtain 1,5-anhydrodulcitol in crystalline form by hydrolysis of the tetraacetate with sodium methylate also failed.

Dibenzalmannitan.[8]—A 30-mg. sample which was obtained from Professor Haas, after one recrystallization from methyl alcohol, melted at 203° and showed a specific rotation of −29.5° ($CHCl_3$, $c = 3.0$). Analysis gave the following values: C, 67.65; H, 5.50, while dibenzalmannitan requires: C, 70.59; H, 5.92. Because of this discrepancy it appears that this sample of dibenzalanhydromannitol contains dibenzalmannitol for which the following composition is calculated: C, 67.1; H, 6.15.

Acknowledgments.—The authors wish to thank Professor Perkin and Professor Haas for samples supplied and Mr. J. F. Alicino for the microanalyses.

Summary

Lead tetraacetate oxidation experiments indicate that styracitol is 1,5-anhydromannitol and polygalitol, 1,5-anhydrosorbitol. Optical superposition calculations support these structures.

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(14) Maurer and Mahn, *Ber.*, **60**, 1316 (1927).

(15) All melting points given in this paper are corrected.

(16) E. Unna, Diss., p. 22, Berlin, 1911; Hudson and Johnson, THIS JOURNAL, **38**, 1227 (1916).

Polygalitol has been isolated from *Polygala senega*.

Aceritol has been proved to be identical with polygalitol.

1,5-Anhydrodulcitol has been prepared and characterized by its crystalline tetraacetate.

NEW YORK, N. Y. RECEIVED JUNE 19, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE PORCELAIN ENAMEL & MFG. CO.]

Automatic Compensation of Flowmeters for Pressure Variations

BY ROGER K. TAYLOR

It frequently happens that it is desired to pass a gas or mixture of gases through an apparatus at a constant rate. When flowmeters are employed in the usual manner, any change in pressure at the flowmeter outlets—such as may follow, for instance, from attachment of other units to the apparatus, or changing resistance to flow offered by contained material, or withdrawal of a sample of gas for analysis—produces a corresponding change in the delivery rates of the flowmeters. Such variation is especially objectionable when dealing with mixtures of gases, as in general there results a change in proportion as well as in total amount of the mixture.

A method of compensating for pressure variations has already been described.[1] However, the compensation is not quite complete, while the device here illustrated does afford complete compensation.

The principles involved will be obvious from the diagram. Tap water enters at "A" and escapes at "B"; the rate of flow is adjusted according to the anticipated rate of pressure variation in the apparatus. Should, for example, the pressure rise, the water level at "B" is correspondingly depressed, and overflow at "B" is interrupted until the level in "C" has risen to an extent corresponding to the pressure change, thus increasing the pressure at the flowmeter inlet and restoring the original delivery rate of the flowmeter. In other words, the pressure drop across the flowmeter depends on the vertical distance from "b" to "c," and is independent of the pressure in the apparatus.

For the sake of simplicity, only one flowmeter is depicted; clearly, however, any number may be accommodated either by having the additional gas-overflow tubes dip into "C," or by attaching at "A" other tubes corresponding to "C" for the other flowmeters.

The overflow tube at "B" must be sufficiently large so that the escaping water will flow down the sides of the tube without trapping gas. It is also advisable to use connecting tubing of rather large bore, to minimize back-pressure from the flowing water.

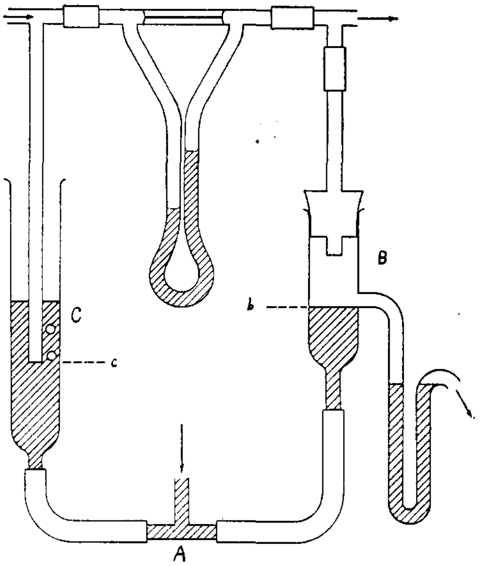

Fig. 1.

If the possible entrance of air bubbles with the tap water into "B" and thence into the apparatus, is undesirable, the water may, of course, be delivered into the top of "C" instead of at "A."

Summary

A device is described for the maintenance of constant delivery rates from flowmeters, irrespective of pressure variations at the flowmeter outlets.

BALTIMORE, MD. RECEIVED APRIL 16, 1937

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(1) Oberfell and Mase, *Ind. Eng. Chem.*, **11**, 294 (1919).