much as 25 g. of crude β-allyl glucoside tetraacetate crystals from absolute ethanol, or 65% of the theoretical. Several batches were combined and purified by recrystallization from hot absolute ethanol to constant rotation. The purified product showed $[\alpha]^{25}\mathrm{D}$ −25.4° in chloroform (*c*, 5.0), −28.2° in methanol (*c*, 5.0); m. p., 88° (cor.). Previously reported values[7] are: $[\alpha]^{17}\mathrm{D}$ −26.4° in methanol; m. p., 89–90°.

Tetra-allyl-β-allyl Glucoside.—This compound was prepared in essentially the same way as the corresponding α-glucoside ether except that the quantities used were based on 39 g. (0.1 mole) of β-allyl glucoside tetraacetate, 50 ml. of methyl ethyl ketone was used as a solvent, and the amount of alkali was increased to take care of the deacetylation. The product, however, required a second treatment with sodium and allyl bromide to bring the allyl content up to the maximum. The distillate from the first step amounted to 28.3 g. containing 3.8 allyl groups per glucose molecule; b. p. at about 0.02 mm., 136–138°; $n^{20}\mathrm{D}$ 1.4799. On the basis of the allyl content, the yield was 85% of the theoretical. The second treatment gave 23 g. of distillate containing 4.7 allyl groups per glucose molecule; b. p. at about 0.03 mm., 125–129°; $n^{20}\mathrm{D}$ 1.4738. The yield was 72% of the theoretical for this step. After a third treatment, the main fraction had the following properties: b. p., 125–128° at 0.01 mm.; $n^{20}\mathrm{D}$ 1.4734; d_{20} 1.0175 g./ml.; molecular refraction, 105.0 (calcd. 104.50); $[\alpha]^{25}\mathrm{D}$ −9.67° for pure substance, −12.9° in ethanol (*c*, 4.1), −13.7° in chloroform (*c*, 4.7); allyl, 53.5% (calcd. for $C_{21}H_{32}O_6$, 53.97%), viscosity at 25°, 16.7 centipoises. The material gelled in 288 minutes at 97°, with oxygen bubbling through it at the rate of 7.5 liters per hour.

Direct Preparation of Penta-allyl Glucose.—Several attempts were made to prepare the allyl ether of glucose directly from the sugar. The best results were obtained by the following procedure: The glucose, 36 g. (0.2 mole), was stirred with 172 ml. of allyl bromide (2.0 moles) in a three-necked flask fitted with an all-glass stirrer, a condenser and a dropping funnel, and heated in a bath at 75°. Sodium hydroxide solution of 50% strength, 176 g. (2.2 moles), was added, very slowly at first, over a period of an hour, after which the reaction was allowed to continue for two hours longer. The mixture was then treated in the same way as the other allyl ethers. Two fractions were obtained. One weighed 4.9 g., boiled at 95–159° at 0.6–0.7 mm., and contained 53.2% allyl or 4.9 allyl groups; the other weighed 4.0 g., boiled at 159–60° at 0.6–0.7 mm., and contained 50.0% allyl or 4.3 allyl groups. Both fractions were yellow liquids. The total distillate was 11% of the theoretical.

Summary

α-Allyl glucoside and galactoside have been prepared in pure state by a modification of Fischer's method. The corresponding penta-allyl ethers have been prepared for the first time from α-allyl glucoside and galactoside and β-allyl glucoside tetraacetate. Also a penta-allyl ether has been prepared directly from glucose. The properties of these compounds are described.

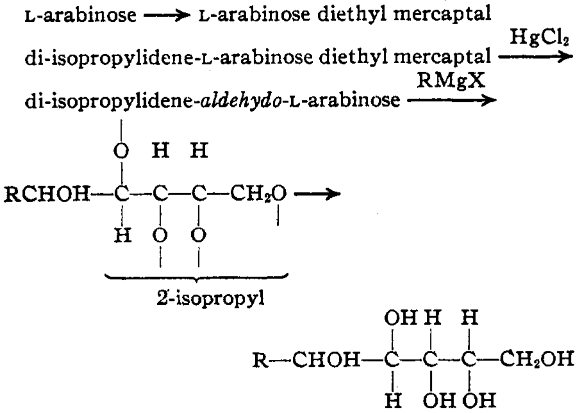
PHILADELPHIA 18, PA. RECEIVED AUGUST 29, 1945

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Synthesis of Some C-Substituted Pentitols

BY JAMES ENGLISH, JR., AND PAUL H. GRISWOLD, JR.

In connection with the preparation of compounds having a structure analogous to that proposed by Kögl[1,2] for the naturally occurring auxins, the possibility of approaching the structures of their side chains by way of the carbohydrate series is being investigated. As a preliminary step in this direction the synthesis of some C-substituted pentitols was carried out. The synthesis, using *aldehydo*-derivatives of L-arabinose, is outlined in the equations:



$$\text{L-arabinose} \longrightarrow \text{L-arabinose diethyl mercaptal}$$

$$\text{di-isopropylidene-L-arabinose diethyl mercaptal} \xrightarrow{\mathrm{HgCl_2}}$$

$$\text{di-isopropylidene-}\textit{aldehydo}\text{-L-arabinose} \xrightarrow{\mathrm{RMgX}}$$

$$\mathrm{RCHOH{-}\underbrace{\overset{\overset{|}{O}}{\underset{H}{C}}{-}\overset{H}{\underset{O}{C}}{-}\overset{H}{\underset{O}{C}}{-}CH_2O}_{\text{2-isopropyl}}} \longrightarrow$$

$$\mathrm{R{-}CHOH{-}\overset{OH}{\underset{H}{C}}{-}\overset{H}{\underset{OH}{C}}{-}\overset{H}{\underset{OH}{C}}{-}CH_2OH}$$

Di-isopropylidine-*aldehydo*-D-arabinose has been successfully condensed with methylmagnesium iodide by Gätzi and Reichstein,[3] and the present work involved analogous reactions with L-arabinose and cyclic Grignard reagents.

The procedure given by Gätzi and Reichstein for the preparation of di-isopropylidene-*aldehydo*-arabinose gave poor yields in our experiments so a study was made of the rate of reaction between derivatives of L-arabinose diethyl mercaptal and mercuric chloride in an effort to improve the yields. Our results confirmed those of Holmberg[4] showing that the reaction, though very slow at room temperature, proceeds faster at 50° than the conditions used by other workers in analogous reactions would indicate.[3,5] It was found also that di-isopropylidene-*aldehydo*-L-arabinose polymerized rapidly and, contrary to the report of Gätzi and Reichstein for the D-isomer, only a small proportion of monomer could be recovered by distillation of the polymer. Accordingly the procedure was modified so as to shorten as much as possible the time required for the preparation and working up of the product.

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[1] F. Kögl, *Z. physiol. Chem.*, **227**, 51 (1934).

[2] J. English and L. J. Lapides, THIS JOURNAL, **65**, 2466 (1943).

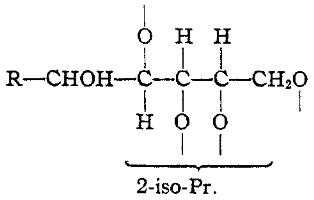
[3] Gätzi and Reichstein, *Helv. Chim. Acta*, **21**, 914 (1938).

[4] Holmberg, *J. prakt. Chem.*, **135**, 57 (1932).

[5] Wolfrom, Weisblat, Zophy and Waisbrot, THIS JOURNAL, **63**, 201 (1941).

Table I

C-Substituted Di-isopropylidene-pentitols



$$R{-}CHOH{-}\overset{\overset{|}{O}}{\underset{H}{C}}{-}\overset{H}{\underset{\underset{|}{O}}{C}}{-}\overset{H}{\underset{\underset{|}{O}}{C}}{-}CH_2O\ |$$

2-iso-Pr.

R—	$[\alpha]^{25}D$ Pyridine	Concn., g./100 cc.	M. p. (cor.), °C.	B. p. (0.01 mm.), °C.	Yield, %	Formula	% Composition C Calcd.	C Found	H Calcd.	H Found
Cyclohexyl	−27.4	3.0	75–76		16	$C_{17}H_{30}O_5$	64.91	64.86	9.55	9.76
Phenyl	−53.0	4.7	79–80	70	20	$C_{17}H_{24}O_5$	66.21	66.27	7.85	7.84
α-Naphthyl	....	...	Sirup	110	72	$C_{21}H_{26}O_5$	70.37	71.45	7.26	6.95

Di-isopropylidine-*aldehydo*-L-arabinose was reacted with phenyl, cyclohexyl and α-naphthyl Grignard reagents. The resulting mixtures of C-substituted pentitols were subjected to repeated recrystallizations to constant melting point and rotation. Except in the case of the phenyl derivative only the least soluble component was isolated.

While the ultimate objective, oxidation of the terminal primary hydroxyl to the corresponding acid for phytohormone investigations, has not yet been realized, a 1-C-cyclohexyl-1,2,3,4-tetraacetyl-5-tritylpentitol has been obtained in crystalline form.

Further studies on the hydrolysis of this trityl derivative and its subsequent oxidation have been temporarily interrupted.

Experimental

Di-isopropylidene-L-arabinose Diethyl Mercaptal.—One-hundred grams of L-arabinose diethyl mercaptal, m. p. 126°,[6] was added to 2000 cc. of dry acetone containing 80 cc. of concentrated sulfuric acid. The suspension was shaken for three hours at room temperature and the acid neutralized either with dry ammonia or sodium carbonate. The acetone was then removed at room temperature from the filtered solution and the product distilled. A yield of 109 g. (83%) was obtained of a light yellow oil, b. p. 110° (0.2 mm.). Molecular distillation gave colorless di-isopropylidene-L-arabinose diethyl mercaptal, $[\alpha]^{26}D$ −79.2° (chloroform). On long standing this slowly decomposes and deposits crystals of the L-arabinose diethyl mercaptal.

Anal. Calcd. for $C_{15}H_{28}O_4S_2$: C, 53.58; H, 8.34. Found: C, 53.56; H, 8.20.

Cleavage of Di-isopropylidine-L-arabinose Diethyl Mercaptal by Mercuric Chloride.—The course of this reaction was followed by titration of the acid liberated according to the equation

$$RCH(SC_2H_5)_2 + 2HgCl_2 + H_2O \longrightarrow RCHO + 2C_2H_5SHgCl + 2HCl$$

The direct titration of hydrochloric acid in the presence of mercuric chloride is unsatisfactory except in the presence of high concentrations of salts such as sodium bromide. Since the addition of such salts to the reaction mixture completely inhibited the above reaction, sodium hydroxide was continuously added to maintain neutrality (methyl red color), aliquots were removed, saturated with sodium bromide, and back-titrated to determine excess base. In order to keep the reaction mixture fluid enough to allow withdrawal of samples, the determinations were carried out in more dilute solution than was used for preparative purposes. The mixture was stirred mechanically in a nitrogen atmosphere throughout the determination.

At room temperature the reaction was found to be very slow, being incomplete after several days. In view of the observed tendency of the free aldehyde to polymerize on standing at room temperature, the temperature was raised to 48–50° to shorten the reaction time. At this temperature 0.79 g. of di-isopropylidene-L-arabinose diethyl mercaptal in 20 cc. of acetone containing 5 cc. of water and 2.4 g. (3.75 moles) of mercuric chloride consumed about 75% of the theoretical quantity of 0.447 *N* alkali in fifteen minutes. Due presumably to some oxidation of the *aldehydo*-arabinose derivative by the excess mercuric chloride, about 110% of the theoretical quantity of alkali was used up by the end of the reaction (about three hours). Since the preparative experiments were run at higher concentrations (see below) it was estimated that a fifteen-minute reaction time would be ample for the production of an optimum yield at this temperature.

Di-isopropylidene-*aldehydo*-L-arabinose.—Freshly precipitated moist cadmium carbonate, 360 g., was heated rapidly to 50° in a solution of 44 g. of di-isopropylidene-*aldehydo*-L-arabinose diethyl mercaptal in 225 cc. of acetone with vigorous stirring in a nitrogen atmosphere. As soon as 50° was reached 148 g. of mercuric chloride in 200 cc. of acetone was added over a period of ten minutes and stirring continued at 50° for five minutes more. The mixture was immediately cooled, diluted with acetone, centrifuged and washed on the centrifuge with the same solvent. After complete removal of acetone from the combined filtrate and washings at room temperature in the presence of fresh cadmium carbonate, the mixture was extracted with chloroform and the extract dried with sodium sulfate. The solvent was removed at room temperature and the residue distilled at low pressure. Yields of 60–80% of colorless liquid di-isopropylidene-*aldehydo*-L-arabinose, b. p. 78° (1 mm.), could be obtained with this procedure. On standing the product polymerized to a glassy mass from which only a small amount of monomer could be recovered by distillation, hence the crude product was used at once in the following reactions.

C-Substituted Di-isopropylidene-pentitols.—Freshly distilled di-isopropylidene-*aldehydo*-L-arabinose was added in ether solution to an excess (2 moles) of a Grignard reagent prepared in the usual manner. After refluxing the reaction mixture for thirty minutes it was added to saturated ammonium chloride solution at ice temperature and the products extracted with ether. The hydrocarbons formed from the excess of Grignard reagent were removed by distillation at 0.05 mm. pressure. The mixture of isomeric 1-C-phenyl-di-isopropylidene-pentitols crystallized on distillation and the corresponding cyclohexyl compound crystallized spontaneously and was not distilled. Both of these crystalline derivatives were crystallized repeatedly to constant rotation and m. p. from light petroleum ether (b. p. 40–60°). The data given in Table I are those of the less soluble isomers obtained in this way. Since the mixture of 1-C-naphthyl-di-isopropylidene pentitols failed to crystallize it was hydrolyzed directly and the free pentitol recrystallized to constant properties.

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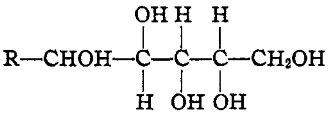
(6) Fischer, *Ber.*, **27**, 673 (1894).

TABLE II

C-SUBSTITUTED PENTITOLS



$$R\text{—CHOH—}\overset{\text{OH}}{\underset{\text{H}}{C}}\text{—}\overset{\text{H}}{\underset{\text{OH}}{C}}\text{—}\overset{\text{H}}{\underset{\text{OH}}{C}}\text{—CH}_2\text{OH}$$

R—	$[\alpha]^{25}\text{D}$ Pyridine	Concn., g./100 cc.	M. p. (cor.), °C.	Yield, %	Formula	% Composition C Calcd.	C Found	H Calcd.	H Found	OH[7] Calcd.	OH[7] Found
Cyclohexyl	+12.6	4.9	148	90	$C_{11}H_{22}O_5$	56.39	56.49	9.47	9.25	36.3	35.7
Phenyl	−37.7	1.0	137	90	$C_{11}H_{16}O_5$	57.88	57.95	7.09	7.07	..	..
Naphthyl	−70.2	3.6	187	5	$C_{15}H_{18}O_5$	64.75	64.70	6.87	6.50	30.6	30.3

C-Substituted Pentitols.—The above 1-C-substituted di-isopropylidene-pentitols were hydrolyzed by refluxing with about 15 volumes of 10% acetic acid for four hours. The clear solutions were evaporated to dryness and the products recrystallized from 95% ethanol to constant rotation and melting point.

The low yield in the case of the 1-C-naphthyl-pentitol is due to the repeated recrystallizations required to separate the mixture of stereoisomers. By a hydrolysis of crude 1-C-phenyl-di-isopropylidine-pentitol and subsequent fractional crystallization from butanol a very small yield of a dextro-rotatory isomer of m. p. 167° was obtained. The amount of material, however, was insufficient to permit purification to constant rotation in this case. This compound was analyzed: *Anal.* Calcd. for $C_{11}H_{16}O_5$: C, 57.88; H, 7.09. Found: C, 57.68; H, 7.25. Since the objective of this work did not require the isolation of both isomers in a pure state at this time, no further efforts were made to characterize the more soluble forms. The properties of the less soluble forms are given in Table II.

1-C-Cyclohexyl-1,2,3,4-tetraacetyl-5-trityl-pentitol.—1-C-cyclohexylpentitol (6.2 g.) was treated at room temperature in dry pyridine solution with one equivalent of triphenylmethyl chloride and allowed to stand overnight. At the end of this time 31 cc. of acetic anhydride was added at ice temperature and the mixture allowed to stand two days. When the reaction mixture was added to ice water, dropwise, the 1-C-cyclohexyl-1,2,3,4-tetraacetyl-5-trityl-pentitol precipitated and could then be crystallized from ethanol. The yield of product of m. p. 134°, $[\alpha]^{25}\text{D}$ −15.0°, pyridine 5.3 g. in 100 cc., was 17.1 g. (90%).

Anal. Calcd. for $C_{38}H_{44}O_9$: C, 70.79; H, 6.88. Found: C, 70.68; H, 6.84.

Summary

Three new crystalline C-substituted pentitols have been prepared from di-isopropylidene-aldehydo-L-arabinose.

NEW HAVEN, CONN.

RECEIVED AUGUST 29, 1945

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(7) Peterson, Hedberg and Christensen, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 225 (1943).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Attempts to Prepare Cyclopolybenzoylenes[1]

BY C. F. KOELSCH AND C. E. BRYAN

If a *p*-phenylene group is a rigid structure with bonds at an angle of 180°, and if attachment of two such groups to a carbon atom does not change the normal carbon valence angle, it should be possible to obtain cyclopoly-*p*-benzoylenes (I) when $n = 5$ or 6, from the corresponding dibasic acids (II). Experiments with this end in view have now been carried out, but with negative results.

$$\underline{\lfloor(COC_6H_4)_n\rfloor}$$

I

$$HO(COC_6H_4)_nCOOH$$

II

Previous data have indicated that the valences joining the phenyl groups with the carbonyl carbon in benzophenone are inclined at an angle of 131–134°[2] (or 122–128°[3]). However, in the present work, no indication was had of the formation of cyclooctabenzoylene[4] when the calcium salt of II, $n = 4$ was pyrolyzed.

Failure to obtain cyclopolybenzoylenes may be a result of either or both of two conditions, each of which tends to be caused by resonance interaction of the linking carbonyl groups with the benzene rings. (1) The acids (II) through resonance alone have more linear structures than would be supposed from previous data[5]; and (2) the benzene rings are co-planar with each other and with the plane containing the bonds linking them to the carbonyl carbon, interference of *o*-hydrogen atoms thus tending to keep the chain nearly linear and rigid.

Experimental[6]

***p_2*-Terbenzone-*p_1,p_3*-dicarboxylic Acid** (II, $n = 3$).[7]—Terephthalic acid (100 g.) and phosphorus pentachloride

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(1) From the Ph. D. Thesis of Carl Eddington Bryan, August, 1942.

(2) Sutton and Hampson, *Trans. Faraday Soc.*, **31**, 945 (1935); Bergmann, Engel, and Mager, *Ber.*, **65**, 446 (1932).

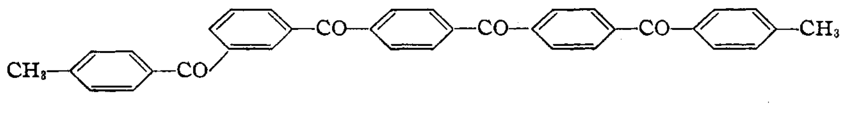
(3) Coomber and Partington, *J. Chem. Soc.*, 1445 (1938).

(4) The angle at the vertex of a regular octagon is 135°.

(5) *Cf.* Lüttringhaus and Buchholz, *Ber.*, **73**, 137 (1940).

(6) Temperatures reported are uncorrected. Those above 300° were measured using a 510° thermometer which showed the b. p. (748 mm.) of mercury to be 358° (literature 356°) and that of sulfur to be 441° (literature 443°).

(7) Application of existing systems of nomenclature to some of the substances prepared leads to awkward names, not conducive to easy visualization. It appeared worthwhile, therefore, in such cases to use a new system for "polybenzones" analogous to the one now used for polyphenyls. *p*-Dibenzoylbenzene thus may be called p_2-terbenzone, p_2 indicating *para* substitution in the second ring; *p*,*p*′-dibenzoylbenzophenone-*p*″,*p*‴-dicarboxylic acid receives the name p_2,p_3-quaterbenzone-p_1,p_4-dicarboxylic acid; the compound



would be named p_1,p_5-dimethyl-m_2,p_3,p_4-quinquebenzone.