times with 75 cc. of water. The isolation of the glyceride from its ether solution and its purification was carried out as described for α-nonanoyl glycerol.

11. **L-α-Dodecanoyl-. 12. L-α-Tetradecanoyl-. 13. L-α-Hexadecanoyl-. 14. L-α-Octadecanoyl Glycerol.**—To the solution of one tenth of one mole of the acetone compound of either one of the four monoglycerides (11–14) in 150 cc. of pure ether, which was cooled to −15° (11, 12) or 0° (13, 14) was added with swirling 150 cc. of concentrated ice-cold hydrochloric acid (*d* 1.19). The solutions, at first homogeneous, soon separated into two layers and, simultaneously, the monoglycerides began to crystallize. After standing for thirty minutes at −15° (11, 12) or 0° (13, 14) 1000 cc. of water was added and the mixtures were again allowed to stand with occasional shaking for thirty minutes at 0°. The monoglycerides were filtered by suction, washed on the filter thoroughly with water and dried *in vacuo* over phosphorus pentoxide. The crude glycerides were recrystallized from low boiling petroleum ether or ether, and dried in a high vacuum.

The physical constants and the analytical data of the α-monoglycerides are reported in Table III.

Verification of the Optical Purity of the α-Monoglycerides by Re-acetonation.—The re-acetonation was carried out by shaking at room temperature a solution of 4.0 g. of the α-monoglyceride in 80 cc. of dry acetone in which 8 g. of anhydrous copper sulfate was suspended. At the end of the third day the acetone solution was decanted, the copper sulfate was washed several times with dry acetone and the combined solutions, after centrifuging, were concentrated by distilling off the acetone under normal pressure at the lowest possible temperature. The residues either on distillation or, as in the case of the hexadecanoyl- and octadecanoyl- glycerol, on recrystallization yielded the acetone α-monoglycerides in analytically pure form. The boiling points, melting points and refractive indices of the acetone monoglycerides obtained by re-acetonation were found to be identical with those of the acetone monoglycerides prepared by acylation of D(+)-acetone glycerol. The good agreement of the specific rotations of the re-acetonated α-monoglycerides with those of the original acetone α-monoglycerides, both of which are reported in Table IV, makes it evident that practically no racemization occurred during acid hydrolysis of the acetone monoglycerides under the conditions described above. This final evidence, taken in conjunction with the other checks, constitutes convincing proof of the optical purity of the α-monoglycerides described in this paper.

TABLE IV

Yields and Specific Rotations of the Acetone Derivatives of Monoglycerides Obtained by Re-acetonation of α-Monoglycerides Containing the Following Acid Radicals.			Original acetone compound $[\alpha]_D$	Loss in rotation, %
	Yield, %	$[\alpha]_D$		
Ethanoyl	88	+1.86°	+1.95°	4.5
Propanoyl	80	+4.4°	+4.66°	5.5
Butanoyl	81	+5.06°	+5.13°	1.3
n-Pentanoyl	90	+5.40°	+5.65°	4.5
Isopentanoyl	90	+5.43°	+5.74°	3.5
Hexanoyl	91	+5.18°	+5.50°	5.5
Heptanoyl	92	+5.22°	+5.20°	0.0
Octanoyl	94	+5.08°	+5.08°	0.0
Nonanoyl	97	+5.22°	+5.22°	0.0
Decanoyl	95	+4.75°	+5.03°	5.5
Hendecanoyl	93	+5.14°	+5.14°	0.0
Dodecanoyl	89	+4.94°	+5.06°	2.4
Tetradecanoyl	98	+4.67°	+4.79°	2.5
Hexadecanoyl	95	+4.86°	+4.95°	1.8
Octadecanoyl	86	+4.78°	+4.94°	3.2

Summary

A homologous series of fourteen optically pure L-α-monoglycerides, containing the normal fatty acids from C_2 to C_{18}, with the exception of C_{13}, C_{15} and C_{17}, has been prepared.

The physical and chemical constants of the L-α-monoglycerides, and of the acetone L-α-monoglycerides, necessary for their synthesis, are recorded.

TORONTO 5, CANADA RECEIVED JUNE 15, 1945

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Allyl Ethers of Carbohydrates. III. Ethers of Glucose and Galactose[1a]

BY E. A. TALLEY, MARY D. VALE AND E. YANOVSKY

A number of allyl ethers of polyhydroxy compounds, including non-reducing carbohydrates, have been prepared.[2] In the work reported here, the corresponding derivatives of two typical reducing sugars, glucose and galactose, were prepared.

Because of their susceptibility to alkali,[3] reducing sugars undergo a number of side reactions in the strongly alkaline solutions used to etherify them and as a result give low yields of a mixture of products. Therefore, we used the glycosides as intermediates.

α-Allyl glucoside has been prepared by the action of α-glucosidase from bottom yeast on glucose and aqueous allyl alcohol.[4] Emil Fischer[5] also reported that the glucoside is formed from allyl alcohol and glucose in the presence of dissolved hydrogen chloride gas, but he gave no details of preparation or properties of the compound formed. α-Allyl galactoside has been prepared by the action of mercuric chloride on galactose benzyl mercaptal[6] in anhydrous allyl alcohol.

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(1a) Prepared for the 1945 Meeting-in-Print, Division of Sugar Chemistry and Technology, American Chemical Society.

(2) P. L. Nichols, Jr., and E. Yanovsky, THIS JOURNAL, **66**, 1625–1627 (1944); **67**, 46–49 (1945); P. L. Nichols, Jr., R. M. Hamilton, Lee T. Smith and E. Yanovsky, *Ind. Eng. Chem.*, **37**, 201–202 (1945).

(3) "Organic Chemistry, Treatise," edited by Henry Gilman, 2nd ed., Vol. II, John Wiley & Sons, Inc., New York, 1943, pp. 1640–1649.

(4) Em. Bourquelot, H. Hérissey and M. Bridel, *Compt. rend.*, **156**, 1493–1495 (1913).

(5) Emil Fischer, *Ber.*, **26**, 2400–2412 (1893).

(6) Eugene Pacsu and Nada Ticharich, *ibid.*, **62B**, 3008–3012 (1929).

β-Allyl glucoside has been prepared by the saponification of the acetate[7] and by the action of emulsin on a solution of glucose in allyl alcohol.[8] β-Allyl glucoside tetraacetate has been prepared by the action of either silver carbonate[7] or silver oxide[9] on acetobromoglucose and allyl alcohol. We prepared the α-glycosides by a modification of the Fischer method.[5] Since these glycosides did not crystallize from the reaction mixture, we extracted them with acetone to obtain crystalline material. β-Allyl glucoside tetraacetate was prepared by the Königs–Knorr reaction as used by Evans and co-workers.[10]

The allyl ethers made from the purified glycosides were colorless liquids. In contrast, the color of the ones prepared from the impure glycosides or directly from glucose ranged from yellow to brown. When distilled, the initial fraction of compounds made from impure glycosides or directly from glucose had a high allyl content, sometimes greater than the theoretical for the pentaallyl compound. Perhaps this was due to the fact that the material contained allyl ethers of breakdown products resulting from the action of the strong alkali on the reducing sugar. The configurational identity of the ethers prepared from the purified glycosides was based on the assumption that the glycosidic allyl group is stable under the conditions of reaction, an assumption that seems to be valid, since little change occurred when a sample of α-allyl glucoside in 40% aqueous sodium hydroxide was heated for five hours at the reaction temperature of 75°. β-Allyl glucoside has been reported to be stable to hot aqueous potassium hydroxide for twenty-four hours,[11] further indicating the stability of these groups. Moreover, the yields were good, and the products were colorless, in contrast with the results obtained with the reducing sugar itself.

In contrast with the glycosides in crystalline form, which are stable to oxygen, their polyallyl ethers are readily gelled by passing oxygen through them, especially at higher temperatures, and they can be converted to hard, transparent insoluble solids by further heating in the presence of oxygen in the same manner as the non-reducing carbohydrate ethers.

Experimental

α-Allyl Glucoside.—This compound was prepared by a modification of the Fischer method.[12] Dry hydrogen chloride gas (24 g.) was dissolved in 800 g. of dry allyl alcohol and then stirred with 400 g. of anhydrous glucose at 70° for four and one-half hours. After cooling, the mixture was treated with 92 ml. of concentrated ammonium hydroxide and then with a decolorizing carbon. The solution was concentrated *in vacuo* to a thick sirup, which was extracted by stirring vigorously with 2-liter portions of dry acetone at room temperature until no more glucoside was removed (eight times). The acetone solutions were concentrated *in vacuo*, seeded and placed in the refrigerator to crystallize. The yield of crude material was 189 g. After recrystallization from acetone containing 1 to 2% water to constant rotation, $[\alpha]^{25}\text{D}$ was +151.1° in water (*c*, 4.7); m. p., 100.5–101.5° (cor.). Previously reported values[4] are: $[\alpha]\text{D}$ +131.7°; m. p. 85–90°.

α-Allyl Galactoside.—The method was the same as that used for the preparation of the glucoside except that the reaction mixture was heated for five and one-half hours at 70° and then for four hours at 80°. The yield of crude product was 115 g. After recrystallization from hot absolute ethanol to constant rotation, $[\alpha]^{25}\text{D}$ was +185.0° in water (*c*, 5.8); m. p., 145–146° (cor.). Previously reported values[6] are: $[\alpha]^{20}\text{D}$ +171.7° (water); m. p. 138–142°.

Tetra-allyl-α-allyl Glucoside.—Purified α-allyl glucoside, 44 g. (0.2 mole), was suspended in 142 g. of 50% aqueous sodium hydroxide (1.76 moles) in a 3-necked flask equipped with a condenser, a dropping funnel and a stirrer. Allyl bromide, 139 ml. (1.6 moles), was added, very slowly at first, over a period of forty minutes, after which the reaction was allowed to proceed for four hours longer. The temperature was maintained at 75° during the addition and reaction time. The reaction mixture was then rapidly steam distilled, the upper layer of the residue was separated, and the water layer was extracted with ether. The ether extract was combined with the upper layer, and the ether was removed *in vacuo*. The residue was distilled from a Claisen flask with a wide-bore delivery tube at 120 to 140°, depending on the rate of distillation under a pressure of 0.03–0.05 mm. The product was colorless, in contrast with that obtained directly from glucose or impure glucoside, which was brown. The distillate (59 g.) contained 49.4% allyl, or 4.2 allyl groups per glucose molecule. On the basis of 4.2 groups, the yield was 85% of the theoretical. The product was then treated with sodium in slight excess of the amount required to react with the remaining hydroxyl groups, and then with a quantity of allyl bromide equivalent to the sodium.[2] The yield was 83% of the theoretical for the second step. The boiling point of the colorless product was 156–157° at 1.0 mm. and 134–135° at 0.03 mm.; $n^{20}\text{D}$ 1.4750; d_{20} 1.0249 g./ml.; molecular refraction, 104.5 (calcd. 104.50); $[\alpha]^{25}\text{D}$ +124.4° (for pure substance), +122.4° in ethanol (*c*, 4.9), +106.5° in chloroform (*c*, 4.9); allyl, 53.4% (calcd. for $C_{21}H_{32}O_6$, 53.97%); viscosity at 25°, 18.4 centipoises. The material gelled in two hundred seventy-four minutes at 97°, with oxygen bubbling through it at the rate of 7.5 liters per hour.

Tetra-allyl-α-allyl Galactoside.—This compound was prepared in the same manner as the corresponding glucoside. The colorless distillate from the first step amounted to 64 g. containing 4.3 allyl groups per galactose molecule; b. p. at 0.01 mm., 125–130°; $n^{20}\text{D}$ 1.4800. Based on a product containing 4.3 allyl groups, the yield was 91% of the theoretical. The second step gave 62.6 g. of distillate, or 91% of the theoretical for this step. The main fraction had the following properties: b. p., 127–128° at 0.1 mm. and 122–123° at 0.01 mm.; $n^{20}\text{D}$ 1.4760; d_{20} 1.0278 g./ml.; molecular refraction, 104.4 (calcd. 104.50); $[\alpha]^{25}\text{D}$ +109.5° (for pure substance), +112.0° in ethanol (*c*, 5.2), +103.8° in chloroform (*c*, 4.7); allyl, 53.9% (calcd. for $C_{21}H_{32}O_6$, 53.97%); viscosity at 25°, 18.9 centipoises. The material gelled in two hundred eighty-three minutes at 97°, with oxygen bubbling through it at the rate of 7.5 liters per hour.

β-Allyl Glucoside Tetraacetate.[10]—A mixture of 58 g. of absolute allyl alcohol (1 mole), 30 g. of silver oxide (0.15 mole), 109 g. of Drierite and 100 ml. of dry, alcohol-free chloroform was stirred for an hour. Then a solution of 41 g. of acetobromoglucose (0.1 mole) in 100 ml. of chloroform was added dropwise over a period of two and one-quarter hours, after which the mixture was stirred for three hours longer. The bromide-free solution yielded as

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[7] Emil Fischer, *Z. physiol. Chem.*, **108**, 3–8 (1919).

[8] Em. Bourquelot and M. Bridel, *Compt. rend.*, **155**, 437–439 (1912); M. Olive, *Soc. Chim. Biol.*, **13**, 254–271 (1931).

[9] Burckhardt Helferich and Joachim Goerdeler, *Ber.*, **73B**, 532–542 (1940).

[10] Delbert D. Reynolds and Wm. Lloyd Evans, THIS JOURNAL, **62**, 66–69 (1940).

[11] Edna M. Montgomery, Nelson K. Richtmyer and C. S. Hudson, *ibid.*, **65**, 3–7 (1943).

[12] Ref. 5; *cf.* Wilfred John Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., London, 1941, p. 176.

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 $[\alpha]^{25}\text{D}$ −25.4° in chloroform (*c*, 5.0), −28.2° in methanol (*c*, 5.0); m. p., 88° (cor.). Previously reported values[7] are: $[\alpha]^{17}\text{D}$ −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°; $n^{20}\text{D}$ 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°; $n^{20}\text{D}$ 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.; $n^{20}\text{D}$ 1.4734; d_{20} 1.0175 g./ml.; molecular refraction, 105.0 (calcd. 104.50); $[\alpha]^{25}\text{D}$ −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

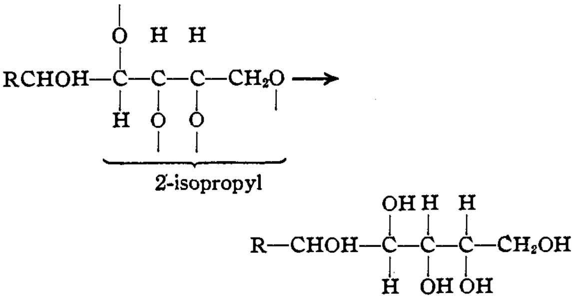
BY JAMES ENGLISH, JR., AND PAUL H. GRISWOLD, JR.

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:

L-arabinose ⟶ L-arabinose diethyl mercaptal

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

di-isopropylidene-*aldehydo*-L-arabinose $\xrightarrow{RMgX}$



$$\text{RCHOH}-\underset{\text{H}}{\overset{\text{O}}{\text{C}}}-\underset{\text{O}}{\overset{\text{H}}{\text{C}}}-\underset{\text{O}}{\overset{\text{H}}{\text{C}}}-\text{CH}_2\text{O} \longrightarrow \quad \underbrace{}_{\text{2-isopropyl}}$$

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

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).