3. Additional proof is brought forward that the viscosity of a starch paste is directly connected with the number of swollen granules (gelatinized) in that paste.

4. The structure of starch pastes has been discussed and it has been shown that its characteristic properties in the case of corn are functions more of the physical nature of the starch granules than of the chemical nature of the amyloses.

5. The results indicate that before a separation of the constituent amyloses in corn starch can be made, all of the granules must be ruptured. This is evidenced by a drop in the viscosity of starch pastes. Any attempts at separation before this point result in fictitiously high results in insoluble material. Although a few granules rupture easily, the great bulk do so only with great difficulty when a paste is made in the ordinary way.

NEW YORK CITY

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON THE REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XX. PREPARATION, PROPERTIES AND IDENTIFICATION OF GLYCEROL BETA-METHYL ETHER

BY HAROLD HIBBERT, MYRON S. WHELEN[1] AND NEAL M. CARTER[2]

RECEIVED SEPTEMBER 13, 1928 PUBLISHED JANUARY 8, 1929

The important role played by glycerol esters and ethers in animal metabolism, industrial processes and organic research has led various investigators to point out the necessity for a reliable characterization of a series of readily identifiable, simple derivatives of glycerol containing substituents definitely located in the α-, β- and α'-positions.

For reasons defined later in this paper, the glycerol ethers are probably the most suitable for the preparation of such a series. Thus Irvine, Macdonald and Soutar[3] proposed the use of glycerol α,β- and α,α'-dimethyl ethers and α- and β-monomethyl ethers for the identification of mixed glycerides. Controlled hydrolysis of glycerides followed by methylation and further hydrolysis, with the aid of the above reference types, would serve to identify the configuration of the original glyceride substituents.

[1] Holder of Bursary from Canadian National Research Council.

[2] Research Fellow, Department of Industrial and Cellulose Chemistry, McGill University, Montreal.

The authors desire to express their appreciation of the facilities afforded them in carrying out this work, on the one hand to the Canadian National Research Council for the gift of a Bursary (M. S. W.) and on the other to The Forest-Products Laboratory of Canada and the Canadian Pulp and Paper Association for valuable assistance.

[3] Irvine, Macdonald and Soutar, *J. Chem. Soc.*, **107**, 342 (1915).

Later, Gilchrist and Purvis[4] attempted to prepare such a series for the identification of the products obtained by the hydrolysis of methylated glycerol glucosides, but were unable to prepare the α,α'-dimethyl and the β-monomethyl ethers. Of the five possible glycerol methyl ethers, the trimethyl,[5] the α,β-dimethyl,[5] α,α'-dimethyl[6] and α-monomethyl[7,8] have been described.

The recent preparation in this Laboratory[9] of the missing member of this series, glycerol β-methyl ether, is thus of considerable interest as it is believed to be the first preparation of a pure *β-ether* of glycerol. For purposes of ready identification, three crystalline derivatives of this have been prepared, the properties of which are summarized in the following table. The corresponding derivatives of the isomeric α-methyl ether are added for comparison.

Derivative	Of glycerol α-methyl ether, m. p., °C.	Of glycerol β-methyl ether, m. p., °C.	Crystallizing medium
Di-*p*-nitrobenzoate	108	155	Ethyl acetate
Di-phenylcarbamate	118–119	102	Benzene-ligroin
p-Nitrobenzylidene acetal	42; 47	106; 139	Methyl alcohol

The di-benzoates appear to be liquids. In the following table a comparison is given of the properties of the glycerol α- and β-methyl ethers.

	Glycerol α-ether	Glycerol β-ether
Boiling point	110–111° (13 mm.)	122–123° (13 mm.)
Refractive index$^{17°}_{D}$	1.4463	1.4505
Density$^{17°}_{4°}$	1.1197	1.1306

Both ethers are readily soluble in water and most organic solvents The constants of the α-ether are those found by Irvine and co-workers,[8] while those of the β-ether are the results obtained in the preparation of the β-ether by three different processes in this Laboratory.[9,10]

Various *β-esters* of glycerol have been described in the literature,[11] such as the β-nitrate,[12] β-phosphate,[13] β-margarate,[14] β-palmitate,[15] β-benzo-

[4] Gilchrist and Purvis, *J. Chem. Soc.*, **127**, 2738–2739 (1925).

[5] Gilchrist and Purvis, *ibid.*, **127**, 2743–2744 (1925).

[6] Zunino, *Atti Accad. Lincei.*, [5] **6**, II, 348 (1897).

[7] Grün and Bockisch, *Ber.*, **41**, 3471 (1908).

[8] Irvine, Macdonald and Soutar, *J. Chem. Soc.*, **107**, 337 (1915).

[9] Hill, Whelen and Hibbert, THIS JOURNAL, **50**, 2235 (1928).

[10] (a) Hibbert and Carter, *ibid.*, **50**, 3120 (1928); (b) Hibbert and Carter, *ibid.*, **50**, 3376 (1928).

[11] In a previous communication, *ibid.*, **50**, 2238 (1928), the statement was made that "glycerol β-methyl ether marks the first definite β-derivative of glycerol to be recorded in the literature." In order to avoid any misunderstanding it should be clearly stated that this remark had reference only to the alkyl ethers of glycerol.

[12] Will, *Ber.*, **41**, 1120–1122 (1908).

[13] Tutin and Hahn, *J. Chem. Soc.*, **89**, 1755 (1906).

[14] Thompson, *Trans. Roy. Soc. Canada*, [iii] **20**, 449 (1926).

[15] Grün, *Ber.*, **43**, 1288 (1910).

ate[16] and others, and many methods have been advanced for the synthesis of mixed glycerides with substituents in various positions for comparison with natural products.[14,17] Recent papers,[18] however, cast considerable doubt on the validity of any method involving the intermediate use of halohydrins, and particularly the α,α'-dichloro- or dibromohydrin utilized in the preparation of most of the above compounds, since the products obtained proved to be not the β-derivative but the corresponding α-isomer, in other words a "group wandering" had occurred.

Thus the failure of Gilchrist and Purvis[5] to obtain α,α'-dimethyl and β-monomethyl ethers of glycerol by methods analogous to those used in preparing the above glycerides and other representatives of the series of ether was attributed by them[4] to a wandering of the halogen or methyl group. Similar wandering of acyl groups has been reported[17b,19] in the interesting investigation carried out by Grün and co-workers.

All of these facts focus attention upon the importance of using glycerol *ethers* as reference compounds for the determination of configuration, since a wandering of an alkyl group has not been observed in this connection. The authors believe that the methods used for the preparation of glycerol β-methyl ether described in this paper are generally applicable for the detection of all β-glycerol ethers and glucosides.

Experimental Part

Preparation of Di-*p*-nitrobenzoate of Glycerol α-Methyl Ether.—The glycerol α-methyl ether used in this experiment was prepared by two methods: (*a*) hydrolysis of 1,2-*iso*propylidene glycerol 1'-methyl ether;[8] and (*b*) interaction of glycerol α-chlorohydrin (Kahlbaum) with a methyl alcoholic solution of sodium methylate. Both preparations yielded an identical di-*p*-nitrobenzoate.

Seven-tenths of a g. of the pure glycerol α-methyl ether was dissolved in 5 g. of dry pyridine and after first heating slightly to start the reaction, 6.5 g. of *p*-nitrobenzoyl chloride was added in small portions; finally, the whole was heated until the product liquefied. It was then allowed to stand at room temperature for eighteen hours. The pasty mass was well stirred with 250 cc. of $N/10$ sulfuric acid solution at 30° to remove the excess pyridine, washed with dilute sodium bicarbonate, finally with water and dried at 100°. Crystallization from hot toluene first deposited a very small amount of a brownish, amorphous powder, m. p. 188°.[20]

The main product was a definite crystalline compound which on recrystallization from hot toluene separated as yellow needles of m. p. 108°; yield practically theoretical.

---

[16] Helferich and Sieber, *Z. physiol. Chem.*, **175**, 311–315 (1928).

[17] (a) Grün, *Ber.*, **54**, 273 (1921); (b) Fischer, Bergmann and Bärwind, *ibid.*, **53**, 1605 (1920); (c) Whitby, *J. Chem. Soc.*, **128**, 1458 (1926); (d) Helferich and Sieber, *Z. physiol. Chem.*, **170**, 31 (1927).

[18] (a) Fischer, *Ber.*, **53**, 1621 (1920); (b) Fairbourne and Foster, *J. Chem. Soc.*, **128**, 3148–3149 (1926).

[19] Grün and Limpacher, *Ber.*, **60**, 147, 151 (1927).

[20] This product is formed when *p*-nitrobenzoyl chloride and pyridine alone are heated. See in this connection Stather, *Ber.*, **57B**, 1392–1393 (1924); Hermans, *Z. physik. Chem.*, **113**, 337 (1924).

Anal. Subs., 0.1527: CO_2, 0.2971; H_2O, 0.0558. Calcd. for $C_{18}H_{16}O_9N_2$: C, 53.48; H, 3.99. Found: C, 53.08, 53.37; H, 4.09, 4.13.

Preparation of Di-*p*-nitrobenzoate of Glycerol β-Methyl Ether.—The glycerol ether used was obtained by the hydrolysis of 1,1′-*p*-nitrobenzylidene glycerol 2-methyl ether, m. p. 106°.[10b] Another sample prepared by hydrolysis of 1,1′-benzylidene glycerol 2-methyl ether yielded an identical di-*p*-nitrobenzoate.

Six-tenths of a gram of the glycerol ether was treated in an exactly similar manner to that above, using 5 g. of dry pyridine and 6 g. of *p*-nitrobenzoyl chloride. Only one product was obtained, which on recrystallization from hot toluene separated as small clusters of orange needles, m. p. 155°; yield almost quantitative.

Anal. Subs., 0.1799: CO_2, 0.3548; H_2O, 0.0661. Subs., 0.2299: N, 13 cc. at 25° and 756 mm. Calcd. for $C_{18}H_{16}O_9N_2$: C, 53.48; H, 3.99; N, 6.93. Found: C, 53.71; H, 4.11; N, 6.74.

Preparation of the Di-phenylcarbamate of Glycerol α-Methyl Ether, $C_6H_5NHCOOCH_2CH(OCONHC_6H_5)CH_2OCH_3$.—One and two-tenths g. of pure glycerol α-methyl ether, b. p. 110–111° (13 mm.), (obtained from the hydrolysis of 1,2-benzylidene glycerol 1′-methyl ether) was mixed with 2 moles of phenyl isocyanate, warmed in a water-bath at 60° for a short time and then allowed to stand for several days at room temperature. The liquid reaction mixture changed to a glassy mass. On further standing white crystals were deposited and the whole mixture became solid. This was dissolved in warm benzene and recrystallized from a mixture of benzene and ligroin, b. p. 80–90° (equal parts), yielding very fine white needles, m. p. 118–119°.

Anal. Subs., 0.1430: CO_2, 0.3279; H_2O, 0.0737. Calcd. for $C_{18}H_{20}O_5N_2$: C, 62.83; H, 5.82. Found: C, 62.53; H, 5.76.

Glycerol α-methyl ether obtained by the hydrolysis of 1,2-*iso*propylidene glycerol 1′-methyl ether, as well as by the action of sodium ethylate on α-monochlorohydrin, yielded the same product with phenyl isocyanate.

Di-phenylcarbamate of Glycerol β-Methyl Ether, $C_6H_5NHCOOCH_2CH(OCH_3)CH_2OCONHC_6H_5$.—One g. of pure glycerol β-methyl ether, b. p. 123° (13 mm.), (obtained from the hydrolysis of 1,1′-benzylidene glycerol 2-methyl ether) was treated with the equivalent amount of phenyl isocyanate in a similar manner. This yielded fine, white needles from benzene-ligroin solution, m. p. 102°.

Anal. Subs., 0.1340: CO_2, 0.3072; H_2O, 0.0722. Calcd. for $C_{18}H_{20}O_5N_2$: C, 62.83; H, 5.82. Found: C, 62.52; H, 6.02.

A mixed melting point determination made with approximately equal quantities of these two di-phenylcarbamates gave a melting point of 90°, showing the non-identity of these two substances.

Preparation of the *p*-Nitrobenzylidene Acetals of Glycerol α- and β-Methyl Ethers.—This condensation is probably more readily and quickly carried out than that of either of the above two types of derivatives. Full details and an explanation of the existence of the two pairs of melting points are found in a previous paper.[10b] A brief description of the method employed, sufficing for a ready recognition of the two glycerol monomethyl ethers, is given below.

One g. of the glycerol methyl ether is heated with 1.5 g. of pure *p*-nitrobenzaldehyde (1:1 molecular proportions) and a small drop of 40% sulfuric acid (as catalyst) for fifteen to twenty minutes at 110–120°, the container being meanwhile connected to a water suction pump giving approximately 15 mm. pressure. The resulting product is dissolved at 20° in 3.5 cc. of methyl alcohol and allowed to cool overnight at 0° or lower.

Glycerol α-methyl ether when thus treated yields a pasty mass which redissolves in the methyl alcohol on warming to room temperature, but which may be obtained in crystalline form by filtering the pasty mass from the solvent at a low temperature and recrystallizing. The product is a mixture of the two isomeric 1,2-*p*-nitrobenzylidene glycerol 1'-methyl ethers. The isomer melting at 47° always tends to crystallize out first in characteristic short, yellowish prisms, while the second isomer (m. p. 42°) separates as white nodules on further cooling.

From the β-methyl ether, on the other hand, the methyl alcohol deposits a mixture of the two markedly crystalline isomeric 1,1'-*p*-nitrobenzylidene glycerol 2-methyl ethers (m. p. 139 and 106°). Recrystallization usually first deposits the higher-melting isomer as gray-white needles but, depending on the amount of solvent used, the lower-melting isomer may simultaneously crystallize as short, white prisms. Although these may be readily separated and identified, the melting point of the mixture (approximately 90°) serves to differentiate the product from that obtained from glycerol α-methyl ether.

Summary

1. The properties of and methods for identifying glycerol β-monomethyl ether are described.

2. The importance of the product as a "type substance" in organic analyses and syntheses is indicated.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE REDUCTION OF PHENYL NAPHTHYL KETONES BY THE BINARY SYSTEM MAGNESIUM + MAGNESIUM IODIDE

BY W. E. BACHMANN AND R. V. SHANKLAND[1]

RECEIVED SEPTEMBER 28, 1928 PUBLISHED JANUARY 8, 1929

Aromatic ketones[2] are reduced by magnesium + magnesium iodide to free radicals, ketyls, which associate to pinacolates. Addition of water to the pinacolate gives the pinacol. By this method various classes of ketones have been reduced to pinacols. We have now studied the reaction between the binary system and ketones containing a naphthyl group.

We have found that both phenyl α-naphthyl ketone and phenyl β-naphthyl ketone are reduced to the corresponding ketyl $\rightleftharpoons$ pinacolate systems. During the reduction green and brown colors are engendered in the solution. These colors disappear when the solution is exposed to air and reappear when air is prevented from entering. Water likewise removes the color, with concomitant formation of the pinacol.

The pinacol produced from phenyl α-naphthyl ketone by Mg + MgI_2 is different from the pinacol produced from the same ketone by zinc + acetic acid.[3] However, we found that the latter isomer (I) may be trans-

---

[1] Holder of the Prescott Fellowship in Organic Chemistry.

[2] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

[3] Compare the reduction of benzaldehyde which gives rise to mesohydrobenzoin (m. p. 134°) and racemic hydrobenzoin (m. p. 119°).