Summary

Nitration of 1,1,1-trichloro-2,2-bis-(*p*-methoxyphenyl)-ethane (methoxychlor) forms 1,1,1-trichloro-2,2-bis-(3-nitro-4-methoxyphenyl)-ethane.

Two independent methods of proof showed that the structure of the nitration product is that indicated in the above name.

1,1-Dichloro-2,2-bis-(3-amino-4-methoxyphenyl)-ethylene and its precursors showed no activity *in vitro* when tested against *M. tuberculosis*.

NEW ORLEANS 15, LOUISIANA RECEIVED APRIL 18, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Racemic Glucose

BY M. L. WOLFROM AND H. B. WOOD

Racemic glucose was described as a sirup by Fischer.[1] Its purported occurrence in jute leaf[2] requires further experimental substantiation. The excellent synthesis of Sowden and Fischer[3] now makes L-glucose a readily available substance. We have succeeded in crystallizing a racemic form of this sugar. Hudson[4] has discussed the possible anomeric forms of a racemic mutarotating sugar and Fletcher and Hudson[5] have shown how these may be distinguished by acylative and crystallographic technics. Applying these criteria to our substance, we find that the X-ray powder diffraction pattern (Table I) for the racemic form of glucose isolated by us, is sensibly identical with the data reported by Sponsler and Dore[6] for anhydrous α-D-glucose. Since enantiomorphs exhibit like patterns, this is definitive proof that the racemic glucose is α-D,α-L-glucose and that it is a racemic mixture and not a true racemic compound. Supporting indirect evidence for this deduction is obtainable by acetylation technics. The racemic glucose was acetylated at low temperature with acetic anhydride and pyridine[7] and the crystalline product was characterized. L-Glucose was employed to prepare its hitherto unknown α and β pyranoid pentaacetates. These were admixed with equal quantities of their enantiomorphs and the crystalline racemic substances were characterized by melting point and X-ray powder diffraction pattern. The data of Table I show that the two racemic pentaacetates have a different crystal structure than is exhibited by either enantiomorph. Therefore α-D,α-L-glucopyranose pentaacetate (m. p. 140.5–141°) and β-D,β-L-glucopyranose pentaacetate (m. p. 125–126°) are true racemic compounds. The former was identical with the product obtained by the low temperature acetylation of the racemic glucose. This is further evidence that the racemic glucose is α-D,α-L-glucopyranose. The required assumption that the ring or anomeric structure of the sugar did not change on acetylation, while eminently probable, is not rigorous and this evidence is therefore equivocal.

TABLE I

X-RAY POWDER DIFFRACTION PATTERNS[a] OF α-D,α-L-GLUCOSE AND OF SEVERAL GLUCOSE PENTAACETATES[b]

		Pyranose pentaacetates							
α-D,α-L-Glucose I-P-S,[c] Å.	I[d]	α-L-Gluco- I-P-S, Å.	I	α-D,α-L-Gluco- I-P-S, Å.	I	β-D,β-L-Gluco- I-P-S, Å.	I	β-L-Gluco- I-P-S, Å.	I
1.22	1	1.82	1	1.77	1	1.58	1	1.47	1
1.28	1	1.85	1	1.86	2	1.65	1	1.58	1
1.34	2	2.02	1	1.92	1	1.68	1	1.62	1
1.37	1	2.08	1	2.12	2	1.77	2	1.81	3
1.49	1	2.16	3	2.22	2	1.83	2	1.85	1
1.59	2	2.25	1	2.32	1	1.92	1	1.90	2
1.63	1	2.30	1	2.47	3	2.04	1	2.01	2
1.68	1	2.40	1	2.56	3	2.11	1	2.06	1
1.79	1	2.49	1	2.76	3	2.30	1	2.11	2
1.87	1	2.59	1	2.96	1	2.62	3	2.18	3
1.91	3	2.84	1	3.10	4	2.76	1	2.34	3
1.95	3	2.88	2	3.27	4	3.07	1	2.44	2
2.06	3	2.95	1	3.54	8	3.39	5	2.55	4
2.15	1	3.05	1	3.90	9	3.57	1	2.95	2
2.24	4	3.14	2	4.35	5	3.82	1	3.07	5
2.46	8	3.32	2	4.70	6	4.04	10	3.36	4
2.56	4	3.57	7	5.36	7	4.47	6	3.51	7
2.89	3	3.91	4	6.25	1	4.71	7	3.99	1
3.13	7	4.21	9	8.05	10	5.18	4	4.17	6
3.30	1	4.42	6			5.61	9	4.44	10
3.49	5	4.80	5			6.95	2	5.23	1
3.94	3	5.12	2			8.17	5	5.59	8
4.29	10	5.47	8			11.05	8	9.94	9
4.70	9	6.22	1						
5.21	4	7.09	1						
6.06	6	9.25	10						
7.40	3								
8.53	4								

[a] Filtered CuK$_\alpha$ radiation, effectively 1.5148 Å.; film exposure two hours; no back reflections observed. [b] Acknowledgment is made to Professor P. M. Harris and Mr. A. L. Foster for assistance in obtaining these data. [c] Interplanar spacings. [d] Relative intensity, estimated visually; 10, strongest band; 1, weakest band.

Experimental

α-D,α-L-Glucose.—Crystalline α-L-glucose (0.5000 g.) was prepared according to the method of Sowden and Fischer[3] and in admixture with a like amount of α-D-glu-

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(1) E. Fischer, *Ber.*, **23**, 2620 (1890).

(2) H. Saha and K. N. Choudhury, *J. Chem. Soc.*, **121**, 1044 (1922).

(3) J. C. Sowden and H. O. L. Fischer, THIS JOURNAL, **69**, 1963 (1947).

(4) C. S. Hudson, *ibid.*, **65**, 1239 (1943).

(5) H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **69**, 1145 (1947).

(6) O. L. Sponsler and W. H. Dore, *ibid.*, **53**, 1639 (1931).

(7) R. Behrend and P. Roth, *Ann.*, **331**, 359 (1904).

cose was dissolved in 100 ml. of warm, absolute methanol. Crystallization was effected on slow solvent removal in a desiccator over sulfuric acid. Pure material was obtained on recrystallization (or elution) from methanol or ethanol and drying was effected under reduced pressure over phosphorus pentoxide at 56°; m. p. 112–113.5°, $[\alpha]^{20}\mathrm{D}$ 0° (no mutarotation). It crystallized as fine needles.

Anal. Calcd. for $C_6H_{12}O_6$: C, 40.00; H, 6.66. Found: C, 39.90; H, 6.72.

α-D,α-L-Glucopyranose Pentaacetate.—α-D,α-L-Glucose (0.200 g.) and 2 ml. of anhydrous pyridine were cooled to 0° and 1.4 ml. of acetic anhydride was added slowly under mechanical stirring while maintaining the same temperature. The suspension was stirred at 0° for twenty hours after which time the solution was poured slowly into 10 ml. of ice and water. The crystalline material was removed by filtration, washed with water and recrystallized from 95% ethanol; yield 0.258 g. (61%), m. p. 140–140.5°. The substance formed complex rhombic crystals.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.22; H, 5.68. Found: C, 49.21; H, 5.75.

This product showed the same X-ray powder diffraction diagram (Table I) as that obtained by recrystallizing equal amounts (0.2000 g.) of the α-D and the below-described α-L-glucose pentaacetate from 95% ethanol; m. p. 141–141.5°, mixed melting point unchanged; m. p. 113–115° on admixture with the below-described β-D,β-L-pentaacetate of m. p. 125–126°.

α-L-Glucopyranose Pentaacetate.—α-L-Glucose[3] (0.40 g.) was acetylated as described above for the α-D,α-L isomer and the crude crystalline product (0.77 g., 89%, m. p. 108–110°) was recrystallized from ethanol-water; m. p. 112–113°, $[\alpha]^{25}\mathrm{D}$ −101° (*c* 4.4, chloroform) in agreement (opposite sign) with those cited by Hudson and Dale[8] for α-D-glucose pentaacetate.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.22; H, 5.68. Found: C, 49.29; H, 5.30.

β-L-Glucopyranose Pentaacetate.—α-L-Glucose[3] (0.20 g.) was heated on a steam-bath with freshly fused sodium acetate (0.12 g.) and acetic anhydride (2.0 ml.) and heating was maintained for two hours after solution, which required about thirty minutes. The crystalline material (0.38 g., 88%, m. p. 130–131°) obtained on pouring the reaction mixture into 20 ml. of ice and water, was recrystallized from 95% ethanol; m. p. 131–132°, $[\alpha]^{25}\mathrm{D}$ −3.9° (*c* 2.9, chloroform) in agreement (opposite sign) with those cited by Hudson and Dale[8] for β-D-glucose pentaacetate.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.22; H, 5.68. Found: C, 49.30; H, 5.32.

β-D,β-L-Glucopyranose Pentaacetate.—Equal amounts (0.1000 g.) of β-D- and β-L-glucose pentaacetate were recrystallized from 95% ethanol; m. p. 125–126°, needles.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.22; H, 5.68. Found: C, 49.60; H, 5.43.

Summary

1. A crystalline form of racemic glucose has been prepared.

2. The crystalline pyranoid pentaacetates of α-L-, β-L-, α-D,α-L- and β-D,β-L-glucose are described.

3. X-Ray powder diffraction diagrams of the above compounds have been obtained.

4. Mild acetylation of the racemic glucose produces α-D,α-L-glucopyranose pentaacetate.

5. The D,L-glucose (m. p. 112–113.5°) described is a racemic mixture of the α-D and α-L forms of glucose, probably pyranoid.

6. The described pyranoid pentaacetates of α-D,α-L- and β-D,β-L-glucose are true racemic compounds.

COLUMBUS, OHIO

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(8) C. S. Hudson and J. K. Dale, THIS JOURNAL, **37**, 1264 (1915).

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

Liquid–Vapor Equilibrium of Ethanol–Methylcyclohexane Solutions

BY CARL B. KRETSCHMER AND RICHARD WIEBE

In two recent publications results on the liquid–vapor equilibria of ethanol–isoöctane[2] and ethanol–toluene[3] solutions were described. The work has now been extended to solutions of ethanol in methylcyclohexane. The only previous measurements on this system are those of Isii,[4] who measured the total vapor pressure at 0 to 30°.

Experimental

The apparatus, method and purification of the ethanol have been described fully in previous articles.[2,3] A commercial grade of methylcyclohexane was fractionally distilled in an efficient column and percolated through a column of silica gel. Facilities for a determination of the freezing point were not available but the physical properties, d^{25}_{4} 0.76496, $n^{25}\mathrm{D}$ 1.42059, are in satisfactory agreement with the values given by Forziati[5] for a sample containing 0.10 mole per cent. impurity, *viz.:* d^{25}_{4} 0.76501, $n^{25}\mathrm{D}$ 1.42056.

Since the densities of the two liquids differ by only 0.02, solutions were analyzed by means of their refractive indices for the green mercury line (5461 Å.). A Bausch and Lomb precision refractometer was used. In order to establish the relation between composition and index of refraction, solutions were made up by weight as previously described.[2] Because of the theoretical and practical interest in the change of volume on mixing, the densities of these solutions were measured as well as their refractive indices. Table I gives the resulting values. The volume changes are all positive and are remarkably close to the values for

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

(2) C. B. Kretschmer, J. Nowakowska and R. Wiebe, THIS JOURNAL, **70**, 1785 (1948).

(3) C. B. Kretschmer and R. Wiebe, *ibid.*, **71**, 1793 (1949).

(4) N. Isii, *J. Soc. Chem. Ind. Japan*, **38**, Sup. Binding, 659 (1935).

(5) A. F. Forziati, A. R. Glasgow, C. B. Willingham and F. D. Rossini, *J. Res. Nat. Bur. Standards*, **36**, 129 (1946).