

with an improved cell $\epsilon_{313 \text{ m}\mu}$ was found to be 0.38 for molar hydrogen peroxide. This is in good agreement with the value 0.39 obtained by Allmand and Style.^{2a}

The author desires to express his appreciation to Professor Farrington Daniels for his help and guidance in this investigation, and to the Research Committee of the University of Wisconsin for substantial aid.

Summary

1. A quantum yield approaching unity as the concentration of hydrogen peroxide is decreased has been obtained for its photolysis in aqueous solution at $28 \pm 2^\circ$ using light of high intensity at $313 \text{ m}\mu$ from a monochromator.

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THE OPTICAL CRYSTALLOGRAPHIC DESCRIPTION OF THE PHENYLOSAZONES AND OTHER DERIVATIVES OF CERTAIN SUGARS¹

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Introduction

The identification of sugars which have been isolated from plants or plant products is a constantly recurring problem. The usual method of attack consists of preparing insoluble derivatives of the sugars in more or less pure crystalline form and identifying these derivatives through their melting points, optical rotation, microscopic observation of crystal form, etc. Since the presence of very small quantities of impurities is sufficient to make melting points misleading, as well as to influence the crystal form, positive identification through these characteristics is sometimes difficult. In searching for some other means, that suggested by Wright,² based on the optical properties of the crystalline derivatives, seemed to offer promise of being such a valuable tool in the identification of sugars that a study of certain derivatives of some of the more common sugars was undertaken.

Materials.—The sugars investigated were glucose, fructose, mannose, galactose, arabinose, xylose and maltose. The derivatives used were the phenylosazones of five of these and the following additional compounds:

¹ This study was carried out under the direction of Dr. H. C. Sampson and Dr. W. G. McCaughey, Departments of Botany and Mineralogy, respectively, The Ohio State University, and presented in partial fulfilment of the requirements of the degree of Doctor of Philosophy to the Faculty of the Graduate School of The Ohio State University. Original manuscript received October 23, 1931.

² Wright, *THIS JOURNAL*, 38, 1647 (1916).

potassium hydrogen saccharate, fructose methylphenylosazone, mannose phenylhydrazone, mucic acid, arabinose diphenylhydrazone and cadmium bromide xylonate. The phenylosazones, potassium hydrogen saccharate and mannose hydrazone were prepared according to Morrow,³ mucic acid and arabinose diphenylhydrazone according to Van der Haar,⁴ fructose methylphenylosazone according to Neuberg,⁵ and cadmium bromide xylonate according to Bertrand and Thomas.⁶

Methods.—The immersion method of examination used by mineralogists and petrographers for many years was employed. The light used in measuring refractive indices and extinction angles was obtained by passing light from a 400-watt Mazda C bulb through two Corning glass ray filters, G584J and G34. These filters transmit light from $540\mu\mu$ to $640\mu\mu$ with a maximum at $580\mu\mu$.

The phenylosazones and several of the other derivatives were obtained as such minute crystals that it was necessary to use an oil immersion objective in measuring the refractive indices.⁷ The size of the crystals, together with the unusually high degree of dispersion shown by the crystals themselves and also by the methylene iodide solutions used in measuring the high indices, made this determination unusually difficult. The indices between 1.70 and 1.80 are accordingly accurate only to about ± 0.005 , while those above 1.80 are accurate to ± 0.01 . The indices below 1.70 are probably all correct within ± 0.002 .

The optical axial angle was estimated from the curvature of the isogyre of an optic axis interference figure or by actual measurement of the distance between the axes, using a micrometer eyepiece. Since, with the equipment available and the type of material under examination, these methods only give approximations, the angles are reported as large, medium or small.

The optical crystallographic data are given in Table I. A determinative table for identification of five of the sugars by optical examination of their phenylosazones is given in Table II.

³ Morrow, "Biochemical Laboratory Methods for Students of the Biological Sciences," John Wiley and Sons, New York, 1927.

⁴ Van der Haar, "Anleitung zum Nachweis zur Trennung und Bestimmung der reinen und aus glucosiden usw. erhaltenen Monosaccharide und Aldehydsäuren," Gebrüder Borntraeger, Berlin, 1920.

⁵ Neuberg, *Ber.*, 35, 959 (1902).

⁶ Bertrand and Thomas, "Practical Biological Chemistry," G. Bell and Sons, London, 1920.

⁷ The immersion media for determining refractive indices below 1.65 were mixtures of a Halowax oil and mineral oil, for indices between 1.65–1.74 mixtures of the Halowax oil and methylene iodide and for those between 1.74–1.86 solutions of iodoform, triiodide of arsenic, triiodide of antimony, tetraiodide of tin and sulfur in methylene iodide prepared according to Merwin, "Media of High Refraction for Refractive Index Determinations with the Microscope; also a Set of Permanent Standard Media of Lower Refraction," *J. Wash. Acad. Sci.*, 3, 35 (1913).

TABLE I
OPTICAL CRYSTALLOGRAPHIC DATA FOR THE PHENYLOSAZONES AND OTHER DERIVATIVES OF CERTAIN SUGARS

Derivative Phenylosazones	Crystal system	Refractive indices			Optical character	Optic axial angle	Sign of elonga- tion	Optical orientation	Crystal habit	Remarks
		α	β	γ						
Glucose	M	1.755	1.780	1.850	+	Medium	\pm	$Y = b$ Axial plane 010	Needles, elongated b flattened 100	Characteristic blue, green, purple inter- ference colors
Galactose	M	1.790	1.800	1.845	+	Small	-	$X \wedge c = 30^\circ$ Axial plane 010	Blades, elongated 100 flattened 100	Orange and green in- terference colors
Arabinose	O	1.760	1.765	1.800	+	Small	+	$Z = Bxa = c$ Axial plane 100	Needles, elongated c flattened 100	Green and yellow in- terference colors
Xylose	O	1.725	1.760	1.805	+	Large	+	$Z = Bxa = c$ Axial plane 100	Needles, elongated c flattened 100	Green and yellow in- terference colors
Maltose	O	1.655	1.715	1.730	-	Small	+	$X = Bxa = b$ Axial plane 100	Blades, elongated c flattened 100	Green, yellow, orange interference colors
Other derivatives										
Potassium hydrogen saccharate	M	1.483	1.571	1.586	-	Medium		$X \wedge c = 42^\circ, Y = b$ Axial plane 010	Tablets, elongated 010 flattened 100	Optic axis nearly \perp 100
Fructose methyl- phenylosazone	O	1.589	1.603	1.82+	+	Small	-	$Z = Bxa = a$ Axial plane 010	Tablets, elongated c flattened 100	Pleochroic, X yellow, Y dark yellow, Z brown
Mannose phenyl- hydrazone	T	1.600	1.650	1.82 \pm	+	Large		Optic axis nearly \perp 001 Axial plane nearly bi- sects acute angle on 001	Rhomb-shaped table- ts lying on 001, in- cluded angles of 106 and 74°	Acute angle some- times truncated by small crystal face
Mucic acid	T	1.490*	1.600	1.610	-	Medium		Axial plane \wedge elonga- tion = 40° $X = Bxa =$ nearly \perp 001	Rhomb-shaped tablets lying on 001, in- cluded angles of 94 and 86°	*Refractive index for α approximate only
Arabinose diphenyl- hydrazone	O	1.627	1.674	1.735	+	Large	\pm	$Z = Bxa = b$ Axial plane \perp 010	Prisms, elongated c	Faces present are prism, brachypinacoid, bra- chydome, macro- dome; sometimes pyramid and basal pinacoid
Cadmium bromide xylonate	O	1.615	1.633	1.638	-	Small	+	$Z = Bxo = c$ Axial plane \perp 110	Prisms, elongated c lying on 110	Bisphenoid faces give characteristic boat shape to crystals.

TABLE II

DETERMINATIVE TABLE FOR IDENTIFICATIONS OF FIVE SUGARS BY OPTICAL EXAMINATION OF THEIR PHENYLOSAZONES

Observation	Sugar is
Immerse substance in liquid with $n = 1.730$	
Two n 's (both crosswise) lower than liquid, = that of third	maltose
One n (crosswise) lower than liquid, other two much greater	xylose
All n 's much higher than liquid, then:	
Immerse substance in liquid with $n = 1.790$	
Two n 's (both crosswise) much lower than liquid, third slightly higher	arabinose
One $n =$ liquid ($\underline{30}^\circ$ with elongation), others higher	galactose
Two n 's less and one much greater, elongation \neq	glucose
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NOTES

The Existence of the High-Temperature Form of Cristobalite at Room Temperature and the Crystallinity of Opal

BY J. W. GREIG

There has appeared recently an interesting letter from Levin and Ott¹ announcing that they have established, by means of x-rays, the existence of the high-temperature modification of cristobalite in a number of opals. So far as I am aware, the high-temperature modification of cristobalite has not before been shown to occur in nature at atmospheric temperatures. In my opinion, however, this form has, contrary to their statement, been shown to be present at room temperature in certain artificial products.

In the course of experimental determinations of points on the liquidus of silica, in systems of silica with other oxides, carried out at this Laboratory, study of the charges frequently shows that some of the cristobalite crystals embedded in the glass are sensibly isotropic, often in contrast to other birefringent ones in the same melt. This has been observed repeatedly by microscopists doing this work here and was explained by Andersen as due to some of the crystals of cristobalite failing to invert during cooling and so persisting in the high-temperature cubic modification.²

In connection with a study of the decomposition of cyanite, $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, at high temperatures to give mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and silica, I have investigated the question of the form in which the silica was present in the product of decomposition.³ When first formed the products of the decomposition are so fine-grained that some question remains as to the nature of the silica, but with continued heating at high temperature it collects

¹ Levin and Ott, *THIS JOURNAL*, **54**, 828 (1932).

² O. Andersen, *Am. J. Sci.*, **39**, 418 (1915).

³ J. W. Greig, *J. Am. Ceram. Soc.*, **8**, 478-481 (1925); *Am. J. Sci.*, **11**, 21-25 (1926).