by Biltz and Wittek.[8] They obtained the same trimethylbarbituric acid by diazomethane treatment of barbituric, 1-methylbarbituric and 1,3-dimethylbarbituric acids. Both nitrogens are thus amenable to methylation by diazomethane, but only one of the methylene hydrogens. To obtain a tetraalkylbarbituric acid with this reagent both of the methylene hydrogens must be previously substituted. The other method in which a symmetrical dialkylurea is used requires a condensation with the acid chloride instead of the ester of the dialkylmalonic acid. Fischer and Dilthey thus prepared the tetraethylbarbituric acid but failed to crystallize it, possibly because of its low melting point. Otherwise its properties were similar to those of the 1,3-dimethyl-5,5-diethylbarbituric acid prepared by both methods and described above.

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[8] Biltz and Wittek, *Ber.*, **54**, 1035 (1921).

Summary

Treatment of 5,5-dialkyl- or 1,5,5-trialkylbarbituric acid with diazomethane in ether solution gives practically quantitative yields of tetraalkylbarbituric acids in which both nitrogens have been methylated. A similar reaction occurs with diazoethane.

The statement of Marotta and Rosanova that the two tautomeric monomethyldialkylbarbituric acids are thus formed is erroneous. The supposed O-methylbarbital which they obtained as a sirup is in reality the low melting di-N-methyl derivative.

DETROIT, MICH.

RECEIVED JUNE 17, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Absorption Edges in the X-Ray Patterns of Native and Mercerized Cellulose

BY WAYNE A. SISSON,[1] GEORGE L. CLARK AND EDWARD A. PARKER[2]

In addition to the spacings of the currently accepted unit cell of cellulose,[3] numerous reports of other long spacings have appeared from time to time in the literature. Spacings of 16.0 and 35.3 Å.;[4] 7.9 or 8.3 Å.;[5] 50.0 Å.;[6,7] 274, 168, 156 and 85 Å.;[8,9] 42.2, 44.9, 66.5 and 83.5 Å.;[10] and 40 to 50 Å.,[11] have been interpreted as being due either to micellar dimensions, or to periodicities larger than the usual diffracting planes of the cellulose unit cell.

The authors[12] recently reported three new "interferences:" two (10.1 and 13.4 Å.) in native cellulose and one (14.2 Å.) in mercerized cellulose, which appear most intense in the pattern when the x-ray beam (Cu K) is parallel to the fiber axis. Regardless of the fibers used, these "spacings" were found to be constant, which indicated that they were not due to non-cellulosic constituents.

With other radiations (Mo, Fe and Cr), the "spacings" were found to vary, while the usual cellulose diffraction lines remained constant, as can be seen by comparing the original negatives of Figs. 1 and 2. The "spacings" were parallel to the 101 and 002 planes in native and the $10\bar{1}$ plane in mercerized cellulose. They were very weak with molybdenum radiation, but increased in intensity with larger values of λ, until with chromium radiation they are almost as intense as the usual diffraction lines. It is the purpose of the present paper to show that these new "spacings" are absorption edges.

It is well known that any element placed in an x-ray beam will absorb to a greater extent those wave lengths just shorter than that element's absorption edges, and on the long wave length side of this edge the x-ray beam will be less affected. If the planes in cellulose diffract general as well as characteristic radiation, definite bromine and silver absorption edges for each plane will appear on the x-ray film which would be similar to and might be mistaken for true diffraction lines.

Since the 002 (3.98 Å.) and 101 (6.10 Å.) planes in native and the $10\bar{1}$ (4.40 Å.) plane in mercerized cellulose diffract characteristic radiation to the greatest degree, they should behave likewise

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[3] K. R. Andress, *Z. physik. Chem.*, **B2**, 380 (1929); **B4**, 190 (1929).

[4] R. O. Herzog and W. Jancke, *Naturwissenschaften*, **16**, 618 (1928).

[5] U. Yoshida and C. Park, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **A17**, 443 (1934).

[6] H. Mark, *Trans. Faraday Soc.*, **25**, 387 (1929).

[7] G. L. Clark, *Ind. Eng. Chem.*, **22**, 474 (1930).

[8] G. L. Clark and K. E. Corrigan, *Radiology*, **15**, 117 (1930).

[9] G. L. Clark and K. E. Corrigan, *Ind. Eng. Chem.*, **23**, 815 (1931).

[10] K. E. Corrigan, Thesis, University of Illinois, 1932.

[11] W. A. Sisson, *Textile Research*, **5**, 119 (1935).

[12] G. L. Clark and W. A. Sisson, Cellulose Symposium, Am. Chem. Soc., Div. Cellulose Chem., N. Y., 1935.

with general radiation. The sin Θ values (λ = 2 d sin Θ) of possible absorption edges corresponding to these planes are given in column 4 of Table I. If, instead of absorption edges, these lines

TABLE I

NATIVE CELLULOSE

Absorption edge		Diffracting planes		Calculated spacings			Observed spacings		
Element	λ	d, Å.	Sin θ	Anticathode	λ	d, Å.	D, cm.	d, Å.	Intensity
Ag	0.484	3.98	0.0608	Mo	0.708	5.82	[a]	[a]	s
Ag	.484	5.40	.0448	Mo	.708	7.90	..	..	
Ag	.484	6.10	.0397	Mo	.708	8.92	0.79	8.88	vw
Br	.918	3.98	.1150	Mo	.708	3.08	2.34	3.11	vw
Br	.918	5.40	.0850	Mo	.708	4.16	..	..	
Br	.918	6.10	.0753	Mo	.708	4.70	[a]	[a]	s
Ag	.484	3.98	.0608	Cu	1.54	12.7	1.20	13.1	w
Ag	.484	5.40	.0448	Cu	1.54	17.2	..	..	
Ag	.484	6.10	.0397	Cu	1.54	19.5	0.80	19.4	vw
Br	.918	3.98	.1150	Cu	1.54	6.7	2.34	6.7	s
Br	.918	5.40	.0850	Cu	1.54	9.1	..	..	
Br	.918	6.10	.0753	Cu	1.54	10.2	1.51	10.3	w
Ag	.484	3.98	.0608	Fe	1.935	15.9	1.22	15.7	vw
Ag	.484	5.40	.0448	Fe	1.935	21.6	..	..	
Ag	.484	6.10	.0397	Fe	1.935	24.3	0.83	23.5	vw
Br	.918	3.98	.1150	Fe	1.935	8.4	2.32	8.5	s
Br	.918	5.40	.0850	Fe	1.935	11.4	..	..	
Br	.918	6.10	.0753	Fe	1.935	12.85	1.51	13.0	w
Ag	.484	3.98	.0608	Cr	2.29	18.85	1.21	19.0	mw
Ag	.484	5.40	.0448	Cr	2.29	25.5	..	..	
Ag	.484	6.10	.0397	Cr	2.29	28.8	0.79	29.1	vw
Br	.918	3.98	.1150	Cr	2.29	9.95	2.33	10.0	s
Br	.918	5.40	.0850	Cr	2.29	13.45	..	..	
Br	.918	6.10	.0753	Cr	2.29	15.2	1.50	15.3	w

[a] Absorption edge superimposed on diffraction line.

TABLE II

MERCERIZED CELLULOSE

Absorption edge		Diffracting spacings		Calculated spacings			Observed spacings		
Element	λ	d, Å.	Sin θ	Anticathode	λ	d, Å.	D, cm.	d, Å.	Intensity
Ag	0.484	4.0	0.0605	Mo	0.708	5.85	..	..	
Ag	.484	4.4	.0550	Mo	.708	6.44	1.14	6.24	s
Ag	.484	7.3	.0331	Mo	.708	10.70	..	..	
Br	.918	4.0	.1145	Mo	.708	3.09	..	..	
Br	.918	4.4	.1043	Mo	.708	3.39	2.12	3.41	s
Br	.918	7.3	.0628	Mo	.708	5.64	..	..	
Ag	.484	4.0	.0605	Cu	1.54	12.75	..	..	
Ag	.484	4.4	.0550	Cu	1.54	14.0	1.14	13.6	w
Ag	.484	7.3	.0331	Cu	1.54	23.25	..	..	
Br	.918	4.0	.1145	Cu	1.54	6.7	..	..	
Br	.918	4.4	.1043	Cu	1.54	7.35	[a]	[a]	s
Br	.918	7.3	.0628	Cu	1.54	12.25	..	..	
Ag	.484	4.0	.0605	Fe	1.935	15.9	..	..	
Ag	.484	4.4	.0550	Fe	1.935	17.5	1.14	17.1	mw
Ag	.484	7.3	.0331	Fe	1.935	29.1	..	..	
Br	.918	4.0	.1145	Fe	1.935	8.4	..	..	
Br	.918	4.4	.1043	Fe	1.935	9.3	2.10	9.3	s
Br	.918	7.3	.0629	Fe	1.935	15.3	..	..	
Ag	.484	4.0	.0605	Cr	2.29	18.9	..	..	
Ag	.484	4.4	.0550	Cr	2.29	20.8	1.14	20.2	vw
Ag	.484	7.3	.0331	Cr	2.29	34.6	..	..	
Br	.918	4.0	.1145	Cr	2.29	10.0	..	..	
Br	.918	4.4	.1043	Cr	2.29	11.1	2.13	10.9	ms
Br	.918	7.3	.0628	Cr	2.29	18.2	..	..	

[a] Absorption edge superimposed on diffraction line.

are interpreted as being due to diffracted monochromatic radiation from the anticathodes listed in column 5, then the spacings to which they would correspond are given in column 7. In column 9 the experimentally observed spacings (assuming monochromatic diffraction) are listed opposite the nearest calculated spacing in column 7. It is readily seen that the observed spacings correspond to calculated absorption edges for the 002 and 101 planes. Similar data for mercerized cellulose appear in Table II.

There are four criteria for testing the validity of the assumption that the "spacings" listed in column 9 of Tables I and II are absorption edges:

(a) That these edges, for a specified specimen to film distance, will remain at exactly the same place on the film regardless of the radiation.

(b) If a "Flurazure" intensifying screen is used there should be no sharp discontinuities at the bromine and silver absorption edges, but a general fogging throughout the whole region.

(c) It will be necessary to have a peak voltage on the x-ray tube of at least 25 k.v. to produce the silver absorption edge and a peak voltage of 13.5 k. v. to produce the bromine edge.

(d) If a strictly monochromatic beam (*i. e.*, the x-ray beam diffracted from the 101 face of a crystal of calcite) is used, absorption edges will not appear.

Experimental

The x-ray tubes used for the various radiations were: copper—Philips Metalix, line focus, electron tube and a Leiss–Siegbahn, self-rectifying, gas tube; iron—Leiss–Siegbahn, self-rectifying, gas tube; chromium—Leiss–Siegbahn, self-rectifying, gas tube and a modified Langsdin–Wyckoff gas tube; molybdenum—Philips Metalix, line focus, electron tube.

For the fiber patterns, the samples consisted of parallel fibers held firmly and compactly together. For the patterns with the x-ray beam parallel to the fiber axis, the fibers were tied in a parallel bundle and then a small cross section—two millimeters in length giving the best results—was cut and fastened to a mount.

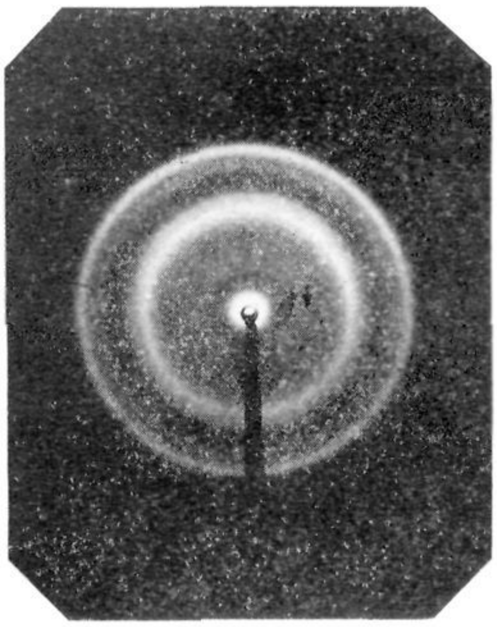

Fig. 1

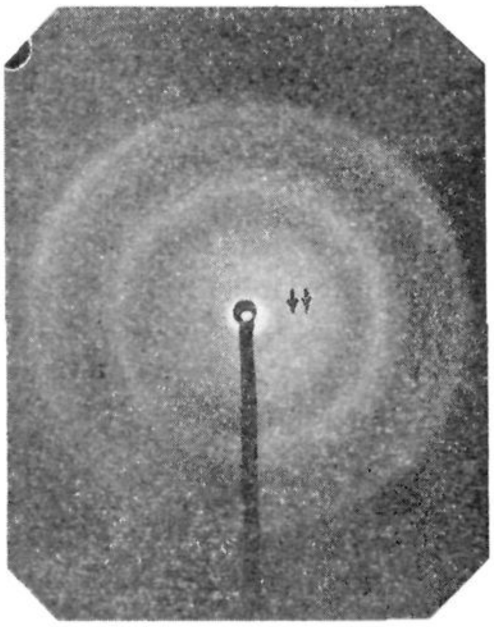

Fig. 2.

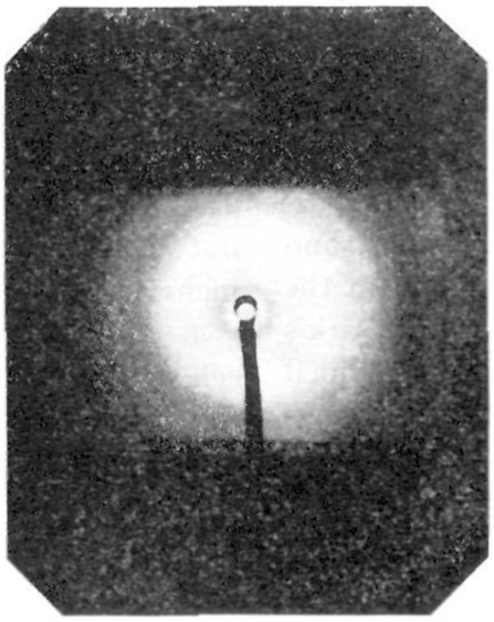

Fig. 3.

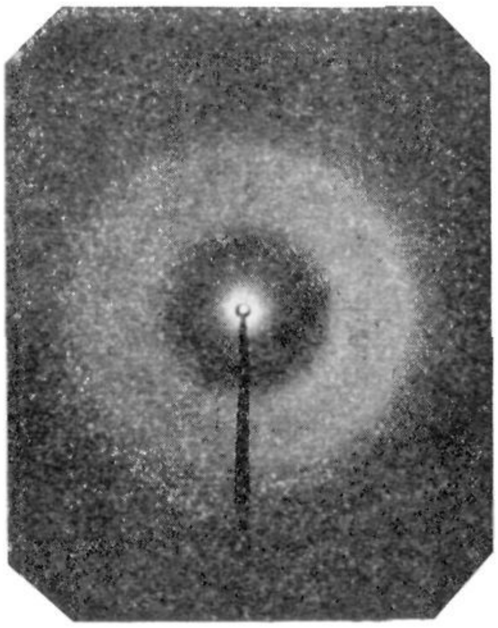

Fig. 4.

1 and 2 show x-ray diagrams of ramie fibers (beam parallel to fiber axis) taken with Cu and Fe radiation, respectively.
3. Same as Figure 2 but with intensifying screen.
4. Same as Figure 1 but with peak 13 k. v. instead of 40 k. v.

With the exception of chromium radiation, where a vacuum camera was used and a specimen to film distance of 4 to 7 cm., all patterns were taken in air and at 5 cm. specimen to film distance.

With iron and copper radiation patterns were taken at peak voltages of 13, 15–24 and 40–60 k. v. At the lowest voltage approximately fifty hours were necessary for the Leiss–Siegbahn tube operating at 2 milliamperes. The Philips copper tube at 25 milliamperes and 13 kilovolts produced patterns in twelve to fifteen hours.

Results

Figures 1 and 2, and column 8 of Tables I and II show how point (a) was fulfilled. All values for column 8 are in centimeters, corresponding to the outer diameter (D) of the absorption edges, and are for a specimen to film distance of 5 cm.

For point (b), a study of two diffraction patterns, shown in Figs. 2 and 3, made under exactly the same experimental conditions with the exception that an intensifying screen was used for Fig. 3, shows that with an intensifying screen the absorption edges are missing, and that the fogging due to the shorter wave lengths is quite noticeable.

For point (c), the silver edge was absent for voltages below 25 k. v., and both bromine and silver below 13.5 k. v. This is illustrated in Figs. 1 and 4.

As for point (d), owing to the experimental difficulties involved, the effect of a strictly monochromatic beam reflected from a calcite crystal was not tried, but when a nickel filter was used with copper radiation the intensity of the absorption edges diminished.

The presence of these absorption edges apparently explains some of the large interferences and micellar dimensions which have appeared in the literature. For example, Yoshida and Park's 100 spacing with iron radiation[5] may be explained as a bromine absorption edge. Likewise, if magnesium and aluminum anticathodes are used, the absorption edges for native cellulose would correspond to 36.2, 55.2, 68.4 and 104.8 Å. for aluminum radiation and 42.9, 65.5, 81.2 and 124.3 Å. for magnesium radiation, and these edges approximate some of the spacings found by Corrigan.[10] They also may explain why Sisson[11] was unable to obtain check results with aluminum and magnesium radiation and also why 15 k. v. was necessary to produce interferences. On the other hand, the micellar spacings of 150 to 280 Å. reported by Clark and Corrigan;[3,9] the 50 Å. spacing found in wood by Mark,[6] which he believed to be the cross-sectional size of the micelle; and the 35.3 and 16.0 Å. reported by Herzog and Jancke,[4] do not correspond to absorption edges.

A small strictly parallel pencil of copper radiation, at a sample to film distance of 15 to 20 cm., has been used successfully to identify spacings up to 200 Å. in protein fibers,[13] but no evidence of correspondingly large spacings was found when the method was applied to cellulose.

Summary

1. Diffracted general radiation from the 002 and 101 planes in native and the $10\bar{1}$ plane in mercerized cellulose produces, on the x-ray negative, well-defined bromine and silver absorption edges which are similar in appearance to diffraction lines.

2. Criteria for distinguishing absorption edges from diffraction lines are discussed.

3. Absorption edges correspond to some, but not all, of the large interferences or micellar dimensions for cellulose reported in the literature.

4. No spacings larger than the cellulose unit cell were found.

URBANA, ILLINOIS RECEIVED JUNE 15, 1936

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[13] G. L. Clark, E. A. Parker, J. A. Schaad and W. J. Warren THIS JOURNAL, 57, 1509 (1935).