with a dropping funnel, stirrer and thermometer, and cooled with an ice–salt-bath. Bromine (3.2 g., 0.02 mole) was then dropped in with stirring over a period of one-half hour. The solution was filtered and the carbon tetrachloride removed under reduced pressure. There remained a dark-colored oil which solidified to a brown solid (crude yield, 4.9 g.). Several recrystallizations from ethanol with activated charcoal treatment afforded 3.7 g. of colorless crystals with a fruity odor, m. p. 92–93°. A mixed melting point with the product of condensation of chloral and 2-bromothiophene gave no depression.

Anal. Calcd. for $C_{10}H_6S_2Br_2Cl_3$: S, 14.08. Found: S, 14.15.

Attempted Condensations.—Attempts were made to condense 2-*t*-octylthiophene, 2,5-*t*-butylthiophene, 2,3,5-trichlorothiophene and 2-benzoylthiophene with chloral using conditions reported above for the successful condensations and also using acetic acid as solvent in the reaction. 2-Benzoylthiophene was unaffected by these reaction conditions, being isolated quantitatively unchanged, while the other thiophene derivatives gave dark oils which we were not able to crystallize or to distill under reduced pressure (1 mm.).

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2-Ethylpyridine and Derivatives

BY EARL C. GREGG, JR., AND DAVID CRAIG

2-Ethylpyridine has been prepared in this Laboratory by two independent methods; the hydrogenation of 2-vinylpyridine and the reaction of methyl iodide with α-picolyl lithium. Nevertheless, derivatives (picrate[1] and mercuric chloride[2]) reported by others for 2-ethylpyridine do not agree in their properties with our derivatives.

Since our methods of preparation appear unequivocal, we believe that previously recorded preparations of this compound have been impure or unauthentic.

Experimental

2-Vinylpyridine[3] was hydrogenated at 60 lb. hydrogen pressure at room temperature over old Raney nickel. One-tenth mole of hydrogen was absorbed by one-tenth mole of 2-vinylpyridine in 35 ml. of alcohol. The hydrogenation product distilled at 70–73° at 50 mm. or 144° at atmospheric pressure, n^{20}_D 1.4978. The picrate melted at 108.5–110° (uncor.) when crystallized from alcohol instead of 187° (uncor.) reported by Bergstrom.[1] It was established that no other picrate forming substance was present.

Analytical

Calculated picric acid content for $C_5H_4O_7N_3 \cdot C_7H_9N$ is 68.1%. Picric acid found by polarographic analysis in 0.1 *N* hydrochloric acid solution is 68.1 ± 0.3%.

The chloroplatinic acid derivative melted at 165–166° (uncor.) as reported by Ladenburg.[2] However, the mercuric chloride derivative melted at 113–114° (uncor.) instead of 103–106° (uncor.) reported by Ladenburg.[2] α-Picolyl lithium was prepared according to Walter.[4]

Dry methyl iodide was added dropwise to the α-picolyl lithium in the reaction flask which was immersed in ice. The resulting ether mixture was extracted with water to remove lithium iodide and some of the unreacted α-picoline. The ether layer was extracted with dilute hydrochloric acid to remove the 2-ethylpyridine and remaining unreacted α-picoline. The hydrochloric acid layer was neutralized and the resulting 2-ethylpyridine was drawn off and steam distilled. The 2-ethylpyridine was dried over anhydrous sodium sulfate and fractionated to remove α-picoline at 77–79° at 80 mm. The picrate from the higher boiling (70–73° 50 mm.) fraction melted at 108.5–110° (uncor.). The mixed melting point of the picrates prepared by the two methods was 108.5–110° (uncor.).

The ultraviolet absorption spectrum of the 2-ethylpyridine prepared above was characteristic of a monoalkyl pyridine.

We wish to acknowledge the measurement and interpretation of the ultraviolet absorption spectrum of 2-ethylpyridine by Laura Schaefgen.

A CONTRIBUTION FROM THE
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(2) A. Ladenburg, *Ber.*, **32**, 44 (1899).

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Small Angle X-Ray Scattering of Various Cellulose Fibers

BY A. N. J. HEYN

The study of diffraction and scattering of X-rays at small angles by various substances has been undertaken only very recently and may be considered negligible in comparison with the studies at larger angles.

Small angles studies of fibrous material have been mainly confined to proteins[1–7] which give *discontinuous* scattering indicating the presence of a large (super-identity) period, inside the large molecules.

Only very preliminary work has been done on scattering of cellulose fibers, although it has been long known that ramie fiber gives a *continuous* small angle scattering.[2,8] Kratky and collaborators (1938–1942)[9,10] recently ventured a quantitative evaluation of the scattering in this material and related the identity period calculated to the size and distance of the cellulose micelles, which they found to be 50–60 Å. Besides ramie they also studied a special regenerated cellulose product derived from viscose. (Other authors[11–14]

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(13) B. E. Warren, *J. Chem. Phys.*, **2**, 551 (1934); *Phys. Rev.*, **49**, 885 (1936).

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used different principles for the evaluation of scattering in other materials.)

The investigation of small angle scattering of many different cellulose fibers by the writer showed the following new facts:

1. Different Angle of Scattering in Different Cellulose Fibers.—The angle of scattering of various cellulose fibers proved to vary considerably. In all cases—with the exposure time used—the scattering was very intense within a small angle from the primary beam, causing almost complete blackening of the film, and decreasing quickly within a short distance at the end of the spot (compare photographs). Therefore the extent of the scattering was sufficiently well defined to be easily measured. For illustration, the angle of intense scattering of some of the fibers investigated is given in the order of smaller angles.

Fiber	Hemp	Flax	Jute	Ramie	Viscose	Merc. Cotton	Cotton
Maximum scattering angle	2°	1°42′	1°35′	1°18′	1°9′	51′	36′
Smallest period in Å.	22	26	27	34	38	51, 5	73
Average period in Å. as calculated from mid-point of scattering	44	51, 5	55	68	73	95	146

Accepting Kratky's assumption regarding the validity of the principle of Bragg's law on scattering of compact structures, the angles given would be related with the minimum size and intermicellar distance of the micelles in these fibers. As a preliminary approximation of the *average* size, the identity period is also calculated from the angle at the midpoint of the scattering zone.

Anyway on the basis of this or other principles[11-14] and in connection with other considerations, the data obtained can be explained by the presence of smaller micelles and probably smaller intermicellar distances in hemp, flax and jute, larger micelles and small distances in ramie and cotton and probably small micelles and large intermicellar distances in viscose (faint scattering).

2. Relation with Orientation of Micelles.—The present studies were carried out by using a pin-hole beam instead of a slit, as used in most of the low angle studies by others. This resulted in a scattering image consisting of a horizontal line on the equator of a definite length on both sides of the primary beam in the case of hemp, jute and flax, the line having the same width over its total length, tapering only somewhat at the end. This can be explained by an orientation of the micelles completely parallel to the long axis of these fibers.

In addition fibers were studied where the fibrils and the micellar axis form an angle with the long axis of the fiber. Fibers were selected with decreasing pitch of the fibrils, namely, of *Sanseviera guinensis*, *Agave heterocantha*, and *Cocos nucifera* (and others). The interesting fact was observed that in all these cases the low angle picture consisted of two lines intersecting at the center of the diagram (primary beam), forming a "*cross*" at an angle, presumably identical with the double angle between the micellar and fiber axis. In *Sanseviera* the angle was about 20°, in *Agave* 45° and in *Cocos* (coir, in which the fibrils make an angle of 45° with the long axis) the two scattering lines intersect at exactly 90° (compare photographs).

This fact is the more remarkable as the "*wide*" angle diffraction pattern in these cases shows a *continuous* 002 arc of increasing extent, without any complete interruption. The low angle picture does not show any such smooth transition or continuity between the intersecting lines of the "cross" and appears to represent only the angle formed by opposite parts of the fibrillar spiral at points where the radius is parallel to the X-ray beam.

Therefore, such small angle studies allow a *direct* clear measurement of micellar orientation in fibers. A full explanation of the phenomenon of "cross formation," as described above, might lead moreover to a deeper insight of the micellar structure of fibers.

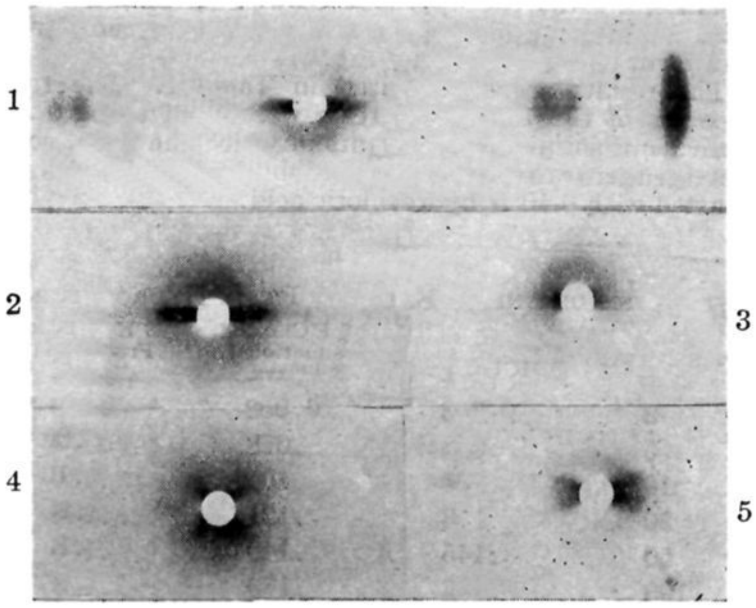

Fig. 1.—Small angle scattering and equatorial wide angle interferences of (1) ramie; (2) jute; (3) mercerized cotton; (4) coir; (5) *Agave heterocantha*. Exposure time, amount of material and distance are the same for all samples.

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Hydrolysis Regeneration of an Anion Exchange Resin

By Hugo P. Kortschak and John H. Payne

No quantitative examination of the regeneration of anion exchange resins by water without the