Found Ag = 63.4 per cent.
Theoretical for $C_2H_3O_2$ Ag = 64.04 per cent.

A solution of these crystals gave no color after diazotization on the addition of dimethyl-α-naphthylamine (no free NH_2-group on the benzene ring). After hydrolysis with dilute hydrochloric acid, the substance gave (by colorimetric method) 80.0 per cent. and 78.8 per cent. of para-aminobenzenesulfonamide. Theoretical for

$CH_3CONHC_6H_4SO_2NH_2$ = 80.3 per cent.

The above data prove the conjugated compound obtained from rabbit's urine to be para-acetylaminobenzenesulfonamide.

This acetyl derivative has been obtained in several other experiments from the urine of rabbits given large doses of the sulfonamide. The following experiment gives a rough idea of the recovery.

A rabbit weighing 1.7 kgm received by mouth 1.7 gms of para-aminobenzenesulfonamide. Ninety cc of urine were secreted in the following 24 hours. This urine was heated just to boiling to dissolve a precipitate, and, while hot, 5 cc were taken and diluted for analysis. From this analysis the remaining 85 cc were calculated to contain 235 mgms of free para-aminobenzenesulfonamide and 1,010 mgms of the conjugated form (calculated as the acetyl compound). The 85 cc of urine were allowed to remain in the ice box for 2 days, the deposited crystals filtered off and dried. Six hundred mgms were obtained. On analysis, these crystals were found to contain 2 per cent. of free sulfonamide and 95 per cent. of the conjugated compound (calculated as the acetyl derivative). After three recrystallizations from water, the compound melted at 218°, and when mixed with para-acetylaminobenzenesulfonamide (the sample which had been identified) melted at 218°. The second 24-hour urine sample contained a considerable amount of the conjugated compound (by colorimetric analysis).

From the urine of a patient being treated with the sulfonamide para-acetylaminobenzenesulfonamide has been isolated and identified.

A 24-hour specimen of urine measured 980 cc. Analysis of a small sample showed it to contain 1.20 gm of free and 1.25 gm of conjugated compound (calculated as acetyl derivative). The urine was treated with 5 gms of charcoal (Norit), shaken and allowed to stand in the ice box for 8 days (a shorter time is sufficient). The charcoal was removed by filtration, and the filtrate analyzed. The filtrate contained 1.03 gm of the free and 0.25 gm of the conjugated compound. The charcoal was treated with 75 cc of 95 per cent. alcohol, heated for a few minutes on a water bath and allowed to stand over night. The charcoal was removed by filtration, the filtrate evaporated to about 15 cc, several volumes of hot water added and the solution placed in the ice box for 4 hours. The crystals obtained by filtration weighed 0.34 gm (dried at 100°). Colorimetric assay showed only a small trace of free sulfonamide, but after hydrolysis the sulfonamide content was increased to 77 per cent. The substance was nearly pure para-acetylaminobenzenesulfonamide. After solution of the 0.34 gm in hot alcohol, hot water was added and the solution was placed in the ice box over night. After recrystallization from water and drying at 90°, the needles melted at 219°, and a mixture of them with the acetyl compound from rabbit's urine melted at 219°. On the colorimetric assay after hydrolysis, the purified compound gave 80.6 per cent. para-aminobenzenesulfonamide, the theoretical being 80.3.

From the urine of another individual receiving the sulfonamide, both the unchanged sulfonamide and the acetyl derivatives were isolated in small amounts by evaporation and fractional crystallization and identified by mixed melting points. This method is laborious and was done before the selective adsorption of the acetyl derivative by charcoal was discovered.

We can conclude that in the rabbit and man the conjugated compound found in the urine after administration of para-aminobenzenesulfonamide by mouth is mainly, if not entirely, the acetylated derivative. It is interesting to note that this is another example of an aromatic compound containing an amino group attached to the benzene ring which the rabbit and man can acetylate but the dog can not.[8]

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DIFFRACTION OF X-RAYS AT VERY SMALL ANGLES BY CELLULOSES AND RAYONS

FROM our laboratory have been reported already the measurements of very large spacings for a number of natural materials. These include 171 A.U. in living nerve,[1] 440 A.U. in collagen, 48 A.U. for radially oriented natural wax in intestinal wall collagen,[2] 81 A.U. in keratin, 58 A.U. in gel rubber and 75 A.U. in chitosan.[3]

By extending the experimental technique to its fullest possibilities, many attempts have been made to resolve interferences at very small angles corresponding to very large spacings in cellulose and its deriva-

[8] J. B. Muenzen, L. R. Cercedo and C. P. Sherwin, *Jour. Biol. Chem.*, 67: 469, 1926.
[1] *Radiology*, 25: 131, 1935.
[2] *Radiology*, 27: 339, 1936.
[3] *Jour. Am. Chem. Soc.*, 57: 1509, 1935; *Jour. Phys. Chem.*, 40: 863, 1935.

tives. In most of these cases there is a definite but somewhat diffuse scattering at very small angles. Equatorial maxima run out from this halo like small arrowheads, but in spite of ingenuity in obtaining the very sharpest possible patterns, it has been impossible to resolve these equatorial streaks into a series of individual spots. There are, however, some very interesting characteristics of this phenomenon which seem worth recording.

Fig. 1*a* is a diagrammatic representation of the

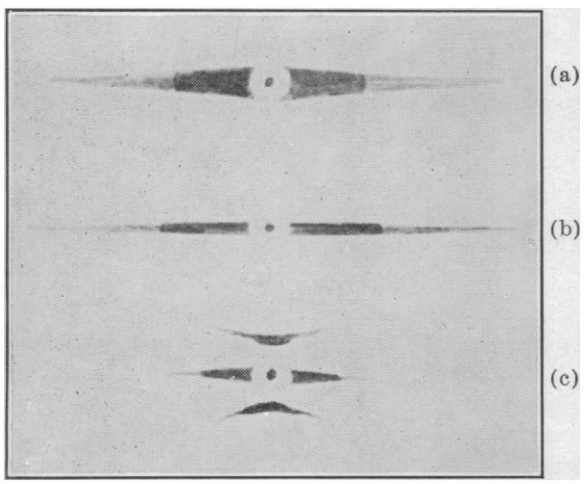

FIG. 1. Diagrams of diffraction effects at very small angles of fiber pattern. (*a*) Native ramie. (*b*) Mercerized ramie dried under tension. (*c*) Regenerated cellulose rayons (nitro, cuprammonium, viscose).

innermost part of a diffraction pattern for native ramie. A continuous streak runs along the equator from the central spot of the pattern, which is widest at the smallest angles and tapers gradually to a nearly constant width of blackening on the film. The greatest intensity seems to be reached at a spacing of about 40 A.U., followed by a rapidly diminishing intensity down to about 20 A.U. The obvious explanation of this pattern seems to be that a whole range of lateral spacings between macromolecules, crystallites or micelles occurs. The greater this spacing is, that is, the smaller the angle, the less perfect is the longitudinal arrangement along the length of the chains in the crystallites so that the resulting diffraction effect is increasingly more diffuse or wider.

In Fig. 1*b* is represented the innermost part of the pattern of mercerized cellulose dried under tension so that the greatest preferred orientation can be gained. The same equatorial streak can be observed as with the original native ramie, but now it is very sharp and uniform in width until it merges with the trace of the undiffracted beam. The marked effect, therefore, of pulling the chains more nearly parallel to each other is directly indicated.

Fig. 1*c* represents an entirely new finding for rayon. With the most careful technique involving very small pinholes, careful blocking of the primary beam, vacuum camera and similar details, we find for all regenerated cellulose rayons, including nitro, cuprammonium and viscose, the production of a very sharp equatorial streak and very definitely a first layer line on either side from which can be measured a fiber identity period of 154 A.U. Acetate rayons do not give this pattern but only a fairly diffuse general scattering around the central spot. The progression in regularity of structure from native ramie to mercerized ramie when dried under tension and then to commercial rayons seems to be clearly indicated by these curious unresolved diffraction maxima at very small angles.

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SECONDARY INCREASE OF LENGTH OF STRETCHED CHILLED RUBBER[1]

DURING some work on "frozen" crude rubber, we have noted that stretched samples behave in a curious way that may have significance in attempts at explaining the rubbery state.

It is well known that crude rubber becomes hard and opaque at low temperatures, and is then said to be "frozen" or "boardy." It exhibits most of the phenomena associated with true crystallization; for instance, a development of well-marked, strongly birefringent granules, a decrease in volume during freezing and an incipient formation of crystal nuclei at a low temperature before contraction in volume begins.

In the current investigation we have noted the following strange behavior of crystallizing samples. When a piece of crude rubber, for example, a strip about 5 mm wide and 2 mm thick, is stretched moderately, cooled to $-25°$ C. and maintained at that temperature, it first becomes hard and then during a few hours the length of the stretched piece increases about 4 per cent. A strip of rubber, stretched and nailed to a board, rises to form an arc between the points of attachment. This secondary elongation is roughly independent of the amount of stretch if the increase in length has been between 20 and 300 per cent. We have observed it with smoked sheet, pale crepe, milled pale crepe and with smoked sheet that has been swelled slightly by benzene to remove strains, and thoroughly dried. It is absent or feeble with vulcanized rubber

[1] Publication approved by the director of the National Bureau of Standards of the U. S. Department of Commerce.