7-acetate obtained previously[6] as shown by the m. p., specific rotation, and absorption spectrum.

Ergostanol-3-one-7 Acetate (IX).—Palladium catalyst (80 mg.) in acetic acid was saturated with hydrogen, and 180 mg. of the trienone VII dissolved in acetic acid was added. In three hours, 33.6 cc. hydrogen (3.5 mols) was utilized. The product was chromatographed on a column of alumina 1 × 18 cm. By elution with 20% benzene in hexane 95 mg. of α-ergostenyl acetate, m. p. 108°, was isolated. By elution with benzene and evaporation of the solvent 75 mg. of residue was obtained which was recrystallized from 80% ethanol, m. p. 183–184°; $[\alpha]^{23}D$ −36 ± 1.5° (0.89% in chloroform).

Anal. Calcd. for $C_{30}H_{50}O_3$: C, 78.55; H, 10.99. Found: C, 78.42; H, 10.90.

The same substance was obtained in 45% yield from $\Delta^{8,9;22,23}$-ergostadienol-3-one-7-acetate (IV) by hydrogenation in acetic acid with palladium. The remainder of the product was α-ergostenol acetate.

On standing with semicarbazide acetate in pyridine–ethanol for three days, a semicarbazone was formed, recrystallized from ethanol, m. p. 225–228°.

Anal. Calcd. for $C_{31}H_{53}O_3N_3$: C, 72.21; H, 10.36; N, 8.15. Found: C, 71.92; H, 10.31; N, 8.18.

The ketone formed a yellow 2,4-dinitrophenylhydrazone, m. p. 216° (decomp.).

Ergostanol-3-one-7.—The acetate IX (30 mg.) was refluxed with 5% potassium hydroxide in methanol for two hours. The product was recrystallized from 80% ethanol, m. p. 154°.

Anal. Calcd. for $C_{28}H_{48}O_2 \cdot H_2O$: C, 77.36; H, 11.59. Found: C, 77.63; H, 11.27.

Treatment of $\Delta^{8,14}$-Ergostenol-3-one-7 Acetate (VIII) with Hydrochloric Acid.—The ketone VIII (40 mg.) was dissolved in 10 cc. ethanol, 0.5 cc. concd. hydrochloric acid was added, and the mixture refluxed for two and one-half hours. The product was reacetylated in pyridine–acetic anhydride and recrystallized from ethanol, m. p. 153°; $[\alpha]^{24}D$ −59 ± 2° (0.46% in chloroform). No double bond isomerization had occurred.

Summary

Mild oxidation of α-dihydroergosteryl acetate with chromic acid yielded only 3 pure products as compared with the six obtained from α-ergostenyl acetate by an identical isolation procedure. Two of these compounds, II and III, are α,β-ketoxides and the third is an α,β-unsaturated monoketone (IV). Only one of the three compounds (III) has a nuclear structure in common with one of the oxidation products of α-ergostenol.

The α,β-unsaturated ketone IV shows selective absorption at 252 mμ, a value in accordance with the generalization of Woodward[8] concerning the most probable $\lambda_{max.}$ value for an α,β,β-substituted, α,β-unsaturated ketone whose carbon–carbon double bond is not exocyclic to any ring. It has been assigned the structure of $\Delta^{8,9;22,23}$-ergostadienol-3-one-7-acetate.

A comparison of the neutral oxidation products obtained from the acetates of α-dihydroergosterol and α-ergostenol leads to the conclusion that α-dihydroergosterol is $\Delta^{8,9;22,23}$-ergostadienol-3.

NEW BRUNSWICK, N. J. RECEIVED MARCH 18, 1943

[CONTRIBUTION FROM THE NEW YORK STATE COLLEGE OF FORESTRY AND DEPARTMENT OF RADIOLOGY, SYRACUSE UNIVERSITY]

X-Ray Studies of Reactions of Cellulose in Non-Aqueous Systems. II. Interaction of Cellulose and Primary Amines[1]

BY W. E. DAVIS,[2] A. J. BARRY,[3] F. C. PETERSON[3] AND A. J. KING

Introduction

The work to be described herein is a natural extension of the earlier investigation of the action of liquid ammonia on cellulose,[4] in which the ammonia-cellulose formed at atmospheric pressure was characterized by the following interplanar spacings: d_{101} = 8.86 Å., $d_{10\bar{1}}$ = 4.47 Å., d_{002} = 4.05 Å. A second ammonia-cellulose derivative was later found[5] to be produced when cellulose is sealed in a glass tube with liquid ammonia at room temperature. The pressure developed in this system is of the order of 10 atmospheres, and under these conditions the derivative has d_{101} = 10.6 Å. This same derivative was also reported by Hess and Gundermann,[6] who found for d_{101} the

(1) Presented before the Cellulose Division of the American Chemical Society at the Buffalo meeting, September 10, 1942.

(2) Present address, Hercules Powder Co., Wilmington, Del. This paper is taken in part from a thesis submitted by W. E. Davis to the Faculty of the New York State College of Forestry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941.

(3) Present address, Dow Chemical Co., Midland, Mich.

(4) A. J. Barry, F. C. Peterson and A. J. King, THIS JOURNAL, **58**, 333 (1936). The structure proposed in this paper for ammonia-cellulose was based on the cellulose unit cell of H. Mark and Kurt H. Meyer, *Z. physik. Chem.*, B2, 115 (1929).

(5) A. J. Barry, A. J. King and F. C. Peterson, informal report before the Cellulose Division of the American Chemical Society at the Chapel Hill, N. C. meeting, April 5–9, 1937.

(6) K. Hess and J. Gundermann, *Ber.*, **70B**, 1788 (1937).

value 10.52 Å., and by Clark and Parker,[7] who found d_{101} = 10.3 Å.

While work on the ammonia-celluloses was still in progress, some preliminary experiments on the action of amines were carried out. The results of this study already have been reported.[8] It was found that cellulose is readily swollen by the lower primary amines, namely, methyl-, ethyl- and propylamines, but that it must be pre-swollen with liquid ammonia before isopropyl-amine or any of the butylamines will produce a change in the X-ray pattern.

The present work was designed principally to confirm the above results on the lower amines, using a somewhat different procedure, and to extend the study to include some of the higher straight-chain primary amines.

Experimental

The cellulose for this work was ramie treated as described in the paper[4] on ammonia-cellulose. The amines, with the exception of hexylamine, were Eastman Kodak Co. products, carefully dried before use. Hexylamine was prepared from heptanoic acid through the amide and purified by fractionation, and the purity was checked by determining the freezing point. Methylamine was purchased as the hydrochloride, the purity of which was checked by analysis for chloride, and the free methylamine was generated and dried as required.

Orientation experiments were carried out with samples wound on spring wire frames as previously described.[4] In this way it was found that for the higher amines (amyl, hexyl and heptyl) the sample can most conveniently be pre-swollen with ethylamine, which is easily removed after immersion of the sample in the higher amine by application of vacuum.

The principal portion of the work was carried out on samples which were sealed in a Pyrex capillary tube with the liquid amine. With methyl- and ethylamines such a procedure results in a certain amount of pressure in excess of atmospheric within the capillary tube, and might be expected to lead to a different degree of swelling than when the treatment is carried out at atmospheric pressure, just as was found with ammonia.[5]

In preparing samples for treatment with higher amines, the procedure was as follows: the sample was sealed in the capillary tube with liquid ethylamine. After allowing sufficient time for complete penetration and swelling to take place, the tube was cooled well below the boiling point of ethylamine, opened, and the upper portion of the tube, which was 7 mm. in diameter, was partly filled with the higher amine. Vacuum was then cautiously applied until there was a noticeable evolution of bubbles. The tube was allowed to warm gradually up to room temperature under moderate vacuum, and kept under vacuum for some time after visible ebullition had ceased. It was then sealed and left for a period sufficient to insure complete swelling. This procedure was used with butyl- and higher amines.

As a source of X-rays, a Phillips-Metallix tube with a copper anode was used. The radiation was unfiltered, and was defined by a pinhole 0.35 mm. in diameter and about 20 mm. long. The tube containing the sample was placed in a camera at a distance of 5 cm. from the film, which was mounted perpendicular to the X-ray beam in a flat film-holder. Diffraction patterns for samples treated with the higher amines were also obtained using a camera with a sample-to-film distance of 15 cm.

Results

The principal equatorial diffractions for normal cellulose are shown diagrammatically in Fig. 1A. The spots progressing outward from the center are designated in the tables as A_1, A_2, etc. The other diagrams, Fig. 1B to 1H, show in proper order diffractions for cellulose swollen with the amines from ammonia to hexylamine. The principal feature of the change in diagram on swelling is an inward transposition of the A_1 spot, the amount of the transposition increasing with increasing chain length of the amine used. The other principal diffractions are shifted somewhat

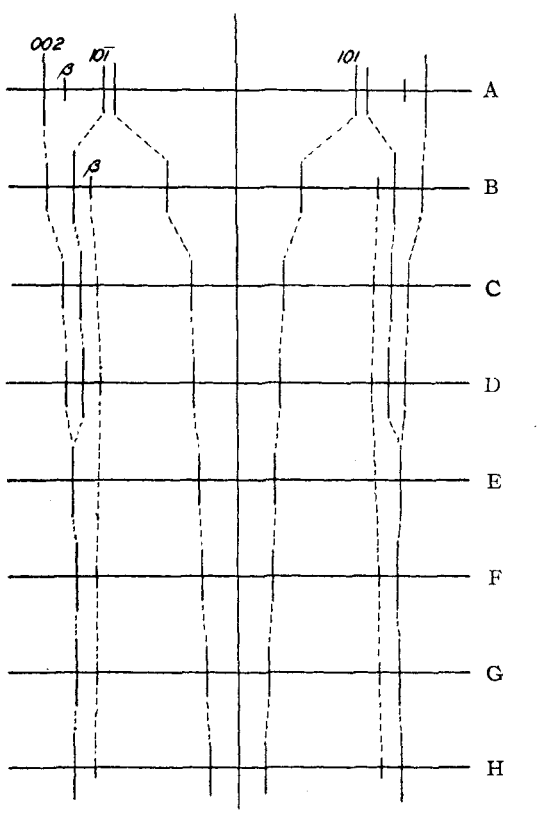


Fig. 1.—Principal equatorial diffractions for amine celluloses.

(7) G. L. Clark and E. A. Parker, *J. Phys. Chem.*, **41**, 777 (1937).

(8) A. J. Barry, A. J. King and F. C. Peterson, Paper presented before the Cellulose Division of the American Chemical Society at the Pittsburgh meeting, September 7–11, 1936.

from their positions in the pattern for normal cellulose, but occupy approximately the same positions for all the amine-swollen celluloses. In these diagrams, the height of a solid line indicates roughly the relative intensity of the corresponding diffraction.

The indices assigned to each spot, and the interplanar distances derived from the measurement thereof, are shown in Table I, which also lists certain weak diffractions not shown in Fig. 1. For the principal equatorial diffractions, the indexing is the same as for ammonia-cellulose.[4] Such a procedure seems most natural in view of the close relationship between ammonia and the amines and the general similarity of all the X-ray patterns obtained. Unfortunately, the many other diffractions available for checking the assignment of indices in the case of ammonia-cellulose appear only very faintly or not at all in the patterns of the amine-celluloses. With propyl- and higher amines even the 002 diffraction is very faint or absent, and the $10\bar{1}$ spot begins to become weak with hexyl- and heptylamines. This is a natural consequence of the increasing separation of lattice points, and the introduction between them of a considerable quantity of material having a relatively uniform distribution of electron density. The 101 diffraction retains virtually the same intensity throughout the series, both because of an actual high electron density in this plane, and because of the decrease in the angle of diffraction from the 101 plane as the size of the amine molecule becomes greater. The only fairly prominent spot not listed in Table I is the meridian diffraction 020, which appears with about the same intensity in all the diagrams, and indicates in every case the same identity period of about 10.3 Å.

Some comment on certain other weak diffractions listed in Table I is required. Some of them correspond to higher orders of 101 as noted in the table. A few spots appear to be bromine absorption edges corresponding to the $10\bar{1}$ diffraction, as described for normal and hydrate cellulose by Sisson, Clark and Parker.[9] The case of propylamine-cellulose is particularly to be noted. This is the highest amine which will swell cellulose without pretreatment, hence the appearance of a few diffractions of normal cellulose is significant in that it indicates that the swelling in this case is not quite complete.

(9) W. A. Sisson, G. L. Clark and E. A. Parker, THIS JOURNAL, **58**, 1635 (1936).

TABLE I

INTERPLANAR SPACING VALUES FOR AMINE-CELLULOSES

FIRST SERIES

Amine	Spot	Indices	Interplanar distance, Å.
NH_3	A_1	101	10.60
	A_2	$10\bar{1}\beta$	4.58
	A_3	$10\bar{1}$	4.60
	A_4	002	3.98
$MeNH_2$	A_1	101	14.67
	A_2	$10\bar{1}\beta$	4.43
	A_3	$10\bar{1}$	4.44
	A_4	002	4.04
$EtNH_2$	A_1	101	15.72
	A_2	$10\bar{1}\beta$	4.63
	A_3	$10\bar{1}$	4.58
	A_4	002	4.23
$PrNH_2$	A_1	101	18.48
	A_2	*a*	8.27
	A_3	*b*	5.92
	A_4	$10\bar{1}$	4.35
	A_5	*c*	3.88
$BuNH_2$	A_1	101	19.73
	A_2	*d*	..
	A_3	*d*	..
	A_4	$10\bar{1}\beta$	4.54
	A_5	$10\bar{1}$	4.49
$AmNH_2$	A_1	101	21.92
	A_2	*e*	10.85
	A_3	*f*	7.55
	A_4	$10\bar{1}\beta$	4.44
	A_5	$10\bar{1}$	4.37
$HeNH_2$	A_1	101	24.85
	A_2	*e*	12.61
	A_3	*f* or *g*	7.93
	A_4	$10\bar{1}\beta$	4.40
	A_5	$10\bar{1}$	4.35
$HpNH_2$	A_1	101	28.74
	A_2	*e*	13.70
	A_3	*g*	9.37
	A_4	*f*	7.81
	A_5	$10\bar{1}\beta$	4.38
	A_6	$10\bar{1}$	4.35

[a] Very weak spot, measurement uncertain. Probably 202. [b] Probably ramie 101. [c] Probably ramie 002. [d] These spots too faint for accurate measurement, origin probably one or more of the causes listed in the other notes. [e] Probably 202. [f] Bromine absorption edge from $10\bar{1}$. [g] Probably 303.

The higher orders of 101 mentioned above may be of value in one respect. The measurement of the 101 diffraction for the higher amines is somewhat uncertain because of the very small values for the angle θ. Thus with amyl- and hexylamines the 202 values check fairly well with those obtained for the 101 diffractions. In the case of heptylamine, the values obtained for 202 and 303 indicate that the true value of d_{101} is probably

closer to 28 Å. than to the figure of 28.74 Å. obtained directly from measurement of the 101 spot.

For comparison with the above data, the *d*-values obtained for cellulose swollen with methyl- and ethylamines at atmospheric pressure are shown in Table II. The value of d_{101} for methylamine-cellulose is seen to be considerably lower, that for ethylamine-cellulose slightly lower than the values for the corresponding derivatives prepared in a closed system at room temperature. The amount of the difference appears to correspond to the difference in pressure involved in working under the two sets of conditions.

TABLE II

INTERPLANAR SPACING VALUES FOR AMINE-CELLULOSES
SECOND SERIES

Amine	Spot	Indices	Interplanar distance, Å.
$MeNH_2$	A_1	101	12.66
	A_2	$10\bar{1}\beta$	4.42
	A_3	$10\bar{1}$	4.42
	A_4	002	4.06
$EtNH_2$	A_1	101	15.28
	A_2	*a*	7.73
	A_3	$10\bar{1}\beta$	4.46
	A_4	$10\bar{1}$	4.43
	A_5	002	4.22
$HeNH_2$	A_1	101	24.0
$HpNH_2$	A_1	101	26.2

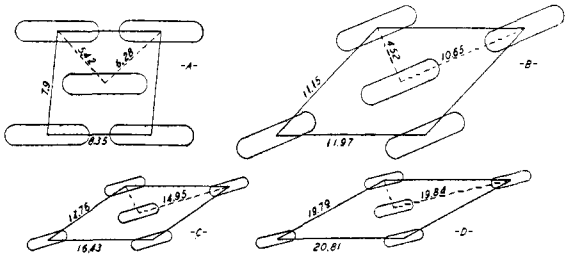
[a] Bromine absorption edge from $10\bar{1}$.

Also included in Table II are values of d_{101} for hexylamine- and heptylamine-celluloses obtained using a sample-to-film distance of 15 cm. As it turned out, this simply meant exchanging a large percentage error in a small measurement for a large absolute error due to diffuseness of the spots obtained with the 15-cm. radius. The value for hexylamine agrees fairly well with that in Table I, but that for heptylamine is considerably lower. In view of the fact that all the measurements were made visually, without the use of a photometer, there does not appear to be any reason to prefer this value to that given in Table I.

A few experiments were also made with ethylenediamine and monoethanolamine. The former readily produced a swollen derivative with a 101 interplanar distance of 11.8 Å., in agreement with the findings of Trogus and Hess.[10] Monoethanolamine was found to have no effect on cellulose unless the latter had been pre-swollen with liquid ammonia, in which case a derivative was formed which had d_{101} = 11.32 Å. This difference in the action of two substances of practically the same molecular dimensions will be taken up in the discussion to follow.

Assignment of indices as described leads to structures for the amine-celluloses of the type shown in Fig. 2, which represents a projection of the unit cell on the 010 basal plane. In view of the greater intensity of the $10\bar{1}$ diffraction as compared with the 002 in the patterns of the amine-celluloses, the glucose residues have been represented as lying in the $10\bar{1}$ plane. The still greater intensity of the 101 diffraction does not controvert this assumed structure, since distension of the lattice in the 101 direction causes a progressive decrease in electron density in the $10\bar{1}$ plane, while, since the $10\bar{1}$ distance is virtually constant, there is no significant decrease in electron density in the 101 plane.

Figure 2 also shows similar projections for normal cellulose and for ammonia-cellulose produced in a closed system at room temperature. Taking into account the smaller scale of the projections of the amine-cellulose structures, the effect of change in chain-length of the swelling agent is readily visualized.



Scale of -A- and -B- twice that of -C- and -D-.

Fig. 2.—Projection of the unit cell on the 010 plane A, normal cellulose; B, NH_3-cellulose; C, $MeNH_2$-cellulose; D, $BuNH_2$-cellulose. Figures are dimensions in Å

The effect of increasing length of the amine molecule is shown in another way in Fig. 3, wherein the 101 interplanar distance is plotted against the number of carbon atoms in the molecule of the amine used. The value for heptylamine has been omitted because of the rather large uncertainty in the measurement of that particular diffraction pattern. For the other amines, it is seen that the increase in the 101 distance does not take place regularly, but exhibits an alternation in amount of increment which is reminiscent of a similar effect notedf or certain interplanar distances in aliphatic acids.[11]

(10) C. Trogus and K. Hess, *Z physik. Chem.*, **B14**, 387 (1931).

(11) S. B. Hendricks, *Chem. Rev.*, **7**, 431 (1930).

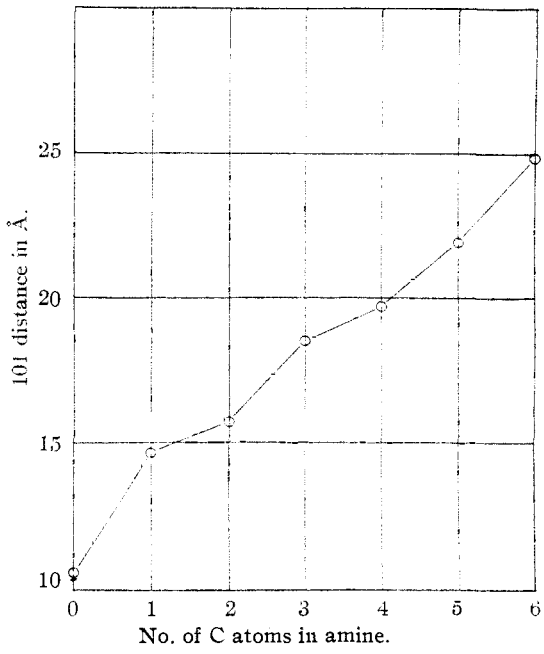


Fig. 3.—Variation in d_{101} with amine chain length.

The average slope of the curve in Fig. 3 is somewhat greater than 2 Å. per amine carbon atom, which indicates that two amine molecules occupy the space between successive 101 planes. Deviation from the slope of 2.53 Å. to be expected for introduction of two additional carbon atoms may be attributed to the positions taken up by the long axes of the amine molecules, which are probably at an angle to the 010 plane rather than lying in it.

Discussion

The mechanism resulting in the transformation of the cellulose probably involves the formation of a hydrogen bridge between the cellulosic hydroxyl group and the amine wherein the hydroxyl hydrogen shares the free electron pair of the amine nitrogen. The swelling process probably starts in the regions of lower orientation within the cellulose breaking the hydrogen bridges involving hydroxyl and possibly acetal oxygens of adjacent glucosidic chains, thus creating a strain which ultimately reaches into the more highly oriented regions and completes the swelling. This process is probably not quite complete, traces of the original structure remaining here and there, as indicated for example by the appearance of faint diffractions of normal cellulose in the X-ray pattern of propylamine-cellulose.

The tremendous distension of the cellulose lattice which takes place on introduction of such large molecules as hexyl- and heptylamines might be expected ultimately to result in dissolution of the cellulose and its dispersion in the respective amine. Failure of such dispersion to take place is undoubtedly connected with the constancy of the $10\bar{1}$ distance for the whole series of amine-celluloses. The constancy of this distance indicates some sort of binding between chains in the $10\bar{1}$ direction, which, as a result of imperfections in the structure, probably brings about a certain amount of cohesion in the 101 direction as well. The nature of this binding in the $10\bar{1}$ direction is not determined by the experiments thus far made, but some of its characteristics can be deduced from the change in structure which takes place on swelling. If, in the amine-swollen derivatives, the glucose residues lie in the $10\bar{1}$ plane, as shown in Fig. 2, then the derivation of this structure from that of normal cellulose requires the rupture of all O—H---O bridges of the original cellulose. Since this process takes place in the presence of an excess of amine, it is to be expected that most, if not all, of the cellulosic hydroxyl groups will have combined with amine molecules. We are then faced with three alternatives. This saturation of the hydroxyl groups may persist, in which case cohesion in the $10\bar{1}$ direction may be due to (a) residual or van der Waals forces, or (b) formation of hydrogen bridges in which an amine nitrogen which has already donated an electron pair to the hydrogen of one hydroxyl group accepts an electron pair from the oxygen of a hydroxyl group of an adjacent chain. This involves the formation of a double bridge of the type O—H---N—H---O. The third alternative, (c), involves the elimination of half the amine molecules, and a resetting up of O—H---O bridges between hydroxyl groups only one of which is bound to nitrogen. This requires the formation of double bridges of the type O—H---O—H---N. We may also recognize the possibility that both (b) and (c) are involved in the structure. It may be pointed out, in connection with the problem of devising experiments to decide among these alternatives, that if the structure is of type (a) or (b) it should be possible to disperse cellulose in a tertiary amine, which is incapable of accepting an electron pair. If the structure is of type (c) or an intermediate type, there should be no dispersion whether the amine be primary, secondary or tertiary.

While formation of O—H---N bridges explains the fact that swelling occurs, it does not explain

the failure of the higher primary amines to swell cellulose directly. From the data available at present, this phenomenon appears to be purely a steric effect. The molecular size of the higher amines prevents their penetrating the cellulose lattice until it has been opened up to a certain extent by treatment with liquid ammonia or one of the lower primary amines. The correctness of this viewpoint is borne out by the fact that even short-chain amines, such as isopropylamine, for example, fail[8] to swell cellulose directly in those cases where the amine molecule is non-linear.

The assumption that the swelling of cellulose by amines is due to formation of hydrogen bridges requires that some explanation be offered for the failure of such bridge-forming compounds as water and alcohols to produce the type of swelling (involving change of X-ray pattern) found for the amines. In this connection it may be pointed out that attachment of water molecules, for example, to the surface hydroxyls of cellulose does not appreciably change the character of that surface. It is still a hydroxylic surface, capable of attaching further water molecules, which therefore do not penetrate farther into the structure. Attachment of amine molecules, on the other hand, does change the character of the surface. Extension of the bridge-forming process therefore requires the gradual penetration of amine molecules into the structure, with consequent change in X-ray pattern.

This picture can be extended to explain the behavior of monoethanolamine as contrasted with that of ethylenediamine. The latter contains only the amine function, and therefore behaves like other amines of the same molecular size (*e. g.*, propylamine), swelling cellulose directly. Attachment of monoethanolamine, however, to the surface hydroxyls of cellulose, whether it be through the hydroxyl or the amino group of the amine, does not change the character of the surface so far as attachment of additional molecules of monoethanolamine is concerned. This explains the failure of monoethanolamine to swell cellulose directly. In the presence of ammonia, we may assume that a N---H—O bridge is formed between the ammonia and the hydroxyl group of the amine, producing a molecular complex which, in its behavior toward the cellulosic surface, is not essentially different from a molecule of diamine. Swelling takes place, and subsequent elimination of ammonia by increasing the temperature produces a structure very similar to that obtained with ethylenediamine, as was to be expected for two molecules of nearly the same size.

A similar explanation may well apply to the observation, reported by Sisson and Saner,[12] that choline, a quaternary ammonium base derived from monoethanolamine, shows no swelling action on cellulose, even though it is as strong a base as the other quaternary hydroxides studied, all of which were found to swell cellulose strongly.

There is one other observation for which no complete explanation can as yet be offered, namely, the fact that the 101 distances found for ammonia-, methylamine- and ethylamine-celluloses depend upon the pressure to which the sample was subjected during X-ray examination. In the case of ammonia-cellulose, the two values found[4,5] for the 101 distance correspond very closely to those to be expected for structures in which either one or two ammonia molecules lie between adjacent 101 planes. This explanation will not hold, however, for the two amine derivatives, since the changes involved are much less than the length of the corresponding amine molecule. It would appear, from the reproducibility of the results, that definite and fairly stable structures must be involved, but no attempt has as yet been made to work them out in detail.

Summary

1. X-Ray study of the action of amines on cellulose has been extended to include the higher straight-chain primary amines up to heptylamine.

2. For the entire series, the 101 interplanar distance has been found to increase with increasing length of the amine molecule.

3. The swelling has been considered as taking place through formation of O—H---N bridges between cellulose and amine.

4. The nature of the binding between chains necessary to account for constancy of the $10\bar{1}$ distance has been discussed, and certain consequences of a few types of binding have been indicated.

5. A steric effect has been adduced to account for failure of the higher amines to swell cellulose directly.

6. An explanation has been offered for the failure of such hydroxyl-containing compounds as water, alcohols and monoethanolamine to swell cellulose.

RECEIVED MARCH 2, 1943

(12) W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **43**, 687 (1939).