

7.7 g. of pure pentaacetyl-*d*-galactonic acid; m. p. 131–132°, $[\alpha]^{25D} +12^\circ$ (*c*, 3; CHCl₃).

Anal. Calcd. for C₁₆H₂₂O₁₂: C, 47.27; H, 5.46; sapon. equiv., 67.7. Found: C, 46.86; H, 5.59; sapon. equiv., 68.6.

Tetraacetyl-*l*-arabonic Acid.—The reaction of tetraacetyl-*l*-arabonamide with nitrous anhydride was carried out in a manner identical with that already described for pentaacetyl-*d*-galactonamide. The anhydrous, crystalline acid was obtained directly, in 73% yield, by removal of the solvent from the chloroform extract. Recrystallization from dry toluene produced pure tetraacetyl-*l*-arabonic acid; m. p. 135–135.5°; $[\alpha]^{25D} -32^\circ$ (*c*, 1.5; CHCl₃). The saponification equivalent was found to be 67.9 (calcd., 66.8).

Anal. (by Mr. S. Cristol). Calcd. for C₁₃H₁₈O₁₀: C, 46.69; H, 5.43. Found: C, 46.82; H, 5.47.

Non-reaction of Nitrous Acid and Pentaacetylgluconamide.—Five grams of the amide in 50 cc. of warm glacial acetic acid was treated dropwise with a solution of 5 g. of sodium nitrite in 20 cc. of water over a period of one hour. The mixture was stirred mechanically and was maintained at 45° during this period. Then it was stirred for two hours more and poured into 200 cc. of ice water. The amide separated at once. More was obtained by neutralizing the solution with sodium bicarbonate. In all, 4.6 g. was recovered (m. p. 187–188°).

Similarly, most of the amide was recovered in the following experiments which were of three to seven hours duration. The amide (5 g.) was dissolved in warm methyl β-hydroxyethyl ether (65 cc.) and to it was added a solution of 13 g. of sodium nitrite in 50 cc. of water. When 25 cc. of 1:1 hydrochloric acid (or an equivalent amount of dilute sulfuric acid) was gradually added to the solution at 40–70°, there was no formation of the desired pentaacetylgluconic acid.

Summary

A general method for the conversion of aldoses into fully-acetylated aldonic acids has been developed. The aldoses are converted in three steps to acetylaldonamides. Treatment of the latter in glacial acetic acid solution with nitrous anhydride gives the corresponding acetylaldonic acids in good yields.

The following new amides and acids related to sugars were prepared: pentaacetyl-*d*-galactonamide, tetraacetyl-*d*-xyloamide, tetraacetyl-*l*-arabonamide, pentaacetyl-*d*-galactonic acid, and tetraacetyl-*l*-arabonic acid.

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An X-ray Study of Stretched Rubber

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Despite the many attacks which have been made upon it, the phenomenon of the stretching of rubber remains only little understood. Because of the tremendous complications involved, the best approach to the problem seems to lie in finding better quantitative data from which to work. Of especial interest during recent years have been the configuration of the molecule and the changes in its shape during stretching and retraction. This paper aims to report some investigations on this subject.

Experimental

There is some hope of learning in full detail the configuration of the molecule in stretched rubber, because stretched rubber gives an X-ray diffraction pattern which shows the material to be mostly crystalline and there is a possibility of solving the crystal structure. This possibility has been explored.

For the present work a cylindrical camera (diameter 94 mm.) was chosen, with the line of stretch of the rubber lying on the cylindrical axis. In order to get as many high order reflections as possible, the sample was cooled in some exposures to about –120°. All samples were of

racked rubber. ("Racking" is stretching to an extensive degree by repeating several times a cyclic process of quick stretching, holding under tension until the sample cools and the stretch "freezes in," and relaxing the stretch in water at about 90°. The X-ray pattern is easily shown to be the same as that of ordinary stretched rubber except that perhaps the "amorphous ring" is reduced in intensity.)²

The best diffraction pattern of a cooled sample was exposed seven hours (at 15 ma.) to copper radiation filtered by nickel foil. A room-temperature exposure of fifty hours was made in which the radiation was monochromatized by reflection from a rock-salt crystal. This film was made especially in the hope of revealing any weak, low-order reflections which might be masked by the general blackening due to the continuous spectrum present in the nickel-filtered radiation.

Inasmuch as more weak, higher order spots were found when the sample was cooled, all numerical data quoted in this paper refer to the low temperature. Table I gives the positions and estimated intensities of all known spots of the fiber diagram (including two "diatropic" points). Positions are indicated by cylindrical coordinates in the Bernal³ reciprocal lattice: ζ , the coordinate parallel to

(1) Feuchter, *Kautschuk*, **2**, 260 (1926).

(2) Hauser and Rosbaud, *ibid.*, **3**, 17 (1927).

(3) Bernal, *Proc. Roy. Soc. (London)*, **A113**, 117 (1926).

the cylindrical axis, which distinguishes the layer lines, and ξ , the radius perpendicular to the cylindrical axis. The values of the radial coordinate are chosen in preference to the more common $\sin \theta/\lambda$, because ξ can be found very easily from the cylindrical films and is most convenient for use in studying the unit cell.

The relative values given in the table should be reliable to within three or four units in the third decimal place for spots on the equator and six or eight units for those on the first and second layer lines. The positions given for spots on the higher layer lines are approximate. The diffuseness and peculiar shape and orientation of the spots make it hard to measure the films very precisely. The absolute values may not be quite as good as the relative ones, because the films were not calibrated carefully enough.

TABLE I
EXPERIMENTAL DATA

Coördinate ξ and intensity are given in body of table. Abbreviations: s, strong; m, medium; w, weak; v, very.

Equator ($\xi = 0$)	First layer line ($\xi = 0.189$)	Second layer line ($\xi = 0.378$)	Third layer line ($\xi = 0.566$)	Fourth layer line ($\xi = 0.755$)
0.254 s	0.220 vw	0 m	0.254 w	
.379 vs	.253 s	0.192 w	.379 m	
.508 sm	.378 s	.254 ms	.508 m	
.717 sm	.417 w	.377 ms	.717 vvw	
1.016 w-	.525 vvw	.419 mw	.758 vw	
1.200 w+	.597 mw	.479 w		
1.270 w	.665 vw	.506 vw		
	.731 w+	.540 mw		
	.766 mw	.595 w	0 m	
	.912 w-	.657 sm	0.379 m	
	.968 w-	.726 ms	.508 w	
	1.018 w-	1.10 w	.717 vw	
	1.270 vvw			

Search for Unit Cell

In the search for a unit cell which is consistent with the positions of all the spots observed, the procedure is to calculate the ξ -values of all reciprocal lattice points for a proposed cell and compare them with the observed values. The correct cell will have a ξ -value equal to every one observed.

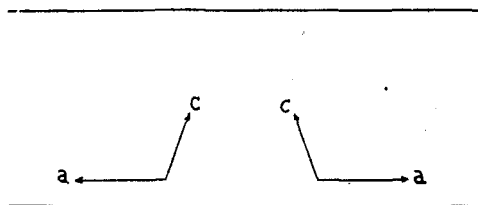


Fig. 1.

A natural first try is the generally accepted cell which was proposed in 1928 by Mark and von Susich.⁴ It is an orthorhombic cell with axes

(4) Mark and von Susich, *Kolloid Z.*, **46**, 11 (1928).

12.3, 8.1 (fiber axis), and 8.3 Å. (The two values 12.3 and 8.3 are twice the plane spacings which give rise to the two very strong equatorial reflections.) For comparison with our table of ξ -values, the values given by Mark and von Susich must be replaced by the corresponding ξ -values, 0.254 and 0.379, from the table. This change makes proper allowance for the fact that the table applies to a cooled sample. With these values assigned, a complete set of ξ -values for the reciprocal lattice of the orthorhombic cell can be computed. It is found that several observed values are not equal, within the experimental error, to any of the computed values. The equatorial reflection at $\xi = 0.717$ is a conspicuous example. Others may be seen in Table II, which includes these data with other possibilities to be described shortly.

A study of all available data shows that two important considerations used in the selection of the orthorhombic cell are correct: the true cell, whatever its form may be, has a fiber axis of length about 8.1 Å. parallel to the direction of stretch and has its other two axes perpendicular to the fiber axis. The further conclusion that these two axes were mutually perpendicular was drawn by Mark and von Susich from a film made in a Weissenberg camera with a very thin strip of rubber which showed a tendency of alignment of its component crystals parallel to the surface of the strip as well as the familiar "fiber" orientation.

The Weissenberg picture does not require this interpretation. Clearly if the a - and c -axes (let us choose the b -axis as the fiber axis) are nearly but not exactly perpendicular, the picture will not be changed. Actually the angle, which we shall call α , may be considerably different from a right angle. To understand this, consider the arrangement in detail. In the sample which has higher orientation there will be a tendency for the a -axes, say, of all the tiny crystals to align themselves parallel to the surface of the sample. When that occurs, the c -axes will align themselves in two groups, one on each side of the perpendicular to the surface of the sample. The two types are indicated in Fig. 1, in which one set of axes belongs to a crystal having its b -axis along the positive direction of stretch; the other, along the negative direction. In any sample there will be many of each type. Now if the a -axes of these many tiny crystals are oriented not exactly parallel to the surface of the strip but only roughly so, in order

that the c -axes will be distributed throughout the range between the two angular positions shown in the figure, then the beams scattered by the sets of planes which include these axes will spread out continuously over quite a range on the Weissenberg film.

That the Weissenberg film of Mark and von Susich has just such a spread opens the possibility that the angle α may be considerably different from 90° . In a determination of the unit cell, the value of α (and of course also the proper indexing of the two independent reflections perpendicular to the fiber axis) remains to be established.

The procedure for an exhaustive study is to assign various sets of indices to these two reflections and in each case calculate the ξ -values of all reciprocal lattice points as a function of the angle α . A range of values from 90 to 115° was considered sufficient to include all reasonable possibilities. Although this calculation was carried through to completion, no thoroughly satisfactory solution for the unit cell was found. Table II gives the dimensions of the two best choices, at room temperature and at the low temperature used. Both have an angle of 109.5° between the sets of planes which reflect the two very strong equatorial spots. The first, which contains sections of eight molecular chains, is just twice as large as the second. While it is consistent with all the diffraction data, it appears too large for the moderate number of spots observed on the film. The second is of the expected size, but does not account for the second layer line spot at $\xi = 0.479$, a spot which is weak but appears to be real. No suitable cell of this size has been found.

TABLE II
DESCRIPTION OF POSSIBLE CELLS

	CELL I (Monoclinic)	
	20°	-120°
a -axis	$26.3 \pm 0.3 \text{ \AA.}$	25.7 ± 0.3
b -axis (fiber)	8.15 ± 0.1	$8.15 \pm .1$
c -axis	8.9 ± 0.1	$8.6 \pm .1$
Monoclinic angle β	109.5°	109.5°
CELL II (Orthorhombic)		
a -axis	12.4 ± 0.1	12.1 ± 0.1
b -axis (fiber)	$8.15 \pm .1$	$8.15 \pm .1$
c -axis	$8.9 \pm .1$	$8.6 \pm .1$

As far as can be determined from the diffraction data, cell I may be described equally well as being the same as cell II with its a -axis doubled. That is, cell I may be considered to be orthorhombic

with axes 24.8, 8.15, and 8.9 \AA. As given, cell I is monoclinic. Its a -axis has the length $24.8/\sin 109.5^\circ$. The monoclinic shape given in the table has been preferred because of certain symmetry considerations.

As a result of this relation between the two choices of cell, number I has twice as many ξ -values as number II in the same range of planar spacings. Among these are included all the ξ -values of cell II.

In Table III are all the measured ξ -values, regardless of the layer line in which they are observed. In the second column are given the nearest calculated values. The value 0.478, which is written in parentheses, belongs only to cell I. All of the others belong to both cells. The third column gives the best fit with the cell, already described, proposed by Mark and von Susich.

Since this work was completed, a recent paper by Lotmar and Meyer⁵ has come to hand. They suggest that the fit is good if the cell of Mark and von Susich is altered by the change of the angle α from 90 to 83.5° . Recalculated for comparison with our data, their best-fitting ξ -values are shown in the last column of Table III. It will be seen that the fit is fairly good except for the two points at 0.540 and 0.729. The discrepancies between these measured values and the nearest calculated ones for the cell of Lotmar and Meyer led us to reject this choice in our study of the

TABLE III
COMPARISON OF CALCULATED AND MEASURED ξ -VALUES

Measd.	Calcd.	Mark, von S.	Lotmar, Meyer
0.192	0.190	0.190	0.190
.220	.219	.228	.215
.254	.254	.254	.254
.379	.379	.379	.379
.418	.421	.426	.414
.479	(.478)	.456	.480
.508	.508	.508	.508
.525	.523	.538	.521
.540	.540	.538	.521
.596	.593	.583	.597
.661	.660	.663	.668
.717	.714	.740	.717
.729	.729	.740	.717
.766	.762	.762	.762
.912	.906	.914	.902
.968	.971	.968	.961
1.016	1.016	1.016	1.016
1.10	1.096	1.083	1.099
1.200	1.199	1.204	1.200
1.270	1.270	1.270	1.270

(5) Lotmar and Meyer, *Monatsh.*, **69**, 115 (1936).

possibilities. They are greater than the probable error of measurement of these two spots.

The indexing of the two strong equatorial spots is shown in Table IV according to the various suggested cells. The column headed "others" gives the indexing of Mark and von Susich and also of Lotmar and Meyer, except that the notation of the former has been altered by the interchange of their *b*- and *c*-axes, to make uniform in the table the assignment of the *b*-axis as the fiber axis.

TABLE IV
INDEXING OF TWO STRONG EQUATORIAL SPOTS

ξ -Value	Cell I	Cell II	Others
0.254	400	200	200
.379	002	102	002

This discussion of the possible unit cell should not be concluded without mention of an interesting consequence of the choice of angle 109.5° between the two strong equatorial spots. It is that the indexing of all the equatorial reflections suggests, insofar as they alone are concerned, an effective subdivision of the cell into smaller units each of which contains only a single molecular chain. If this is correct, it probably means that the pattern formed by the projections of the atoms of a molecular chain upon the base plane will be identical for all the chains actually included in the cell and that these patterns will be oriented similarly and will be centered on a regular two-dimensional lattice with axes of $6.6 (=26.3/4)$ and $4.45 (=8.9/2)$ Å. lying at an angle of 109.5° .

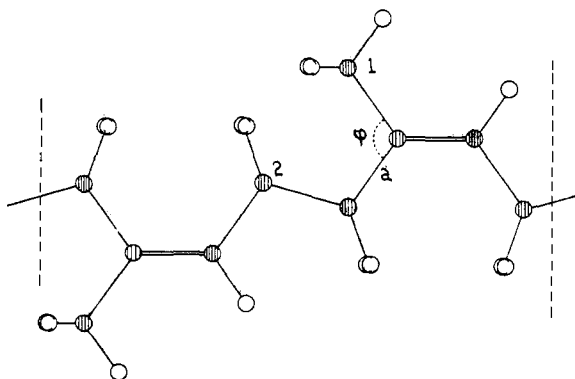


Fig. 2.—The structural formula of rubber: shaded circles represent carbon atoms; open circles, hydrogen atoms; overlapping open circles represent two hydrogen atoms, one above the other.

The Crystal Density.—A further result from the X-ray analysis deserves attention: the density

of crystalline, stretched rubber as calculated from the unit cell. When the angle between the two important sets of planes changes from 90° , the calculated density decreases from the 90° value and comes into better agreement with the best directly measured value. At 109.5° the calculated density is about 1.00. This is much closer to the experimental result of around 0.96 than the calculated value 1.06 for the cell of Mark and von Susich. The cell proposed by Lotmar and Meyer leads to the value 1.05 (calculated from our planar spacing data).⁶

Thus the cells proposed in this paper appear to resolve satisfactorily a discrepancy which has caused a great deal of discussion.

The Configuration of the Molecule

Disappointed in the hope of solving the crystal structure, we must approach the study of the configuration of the molecule with less complete data than we should have liked. However, the X-ray evidence is clear upon the one point that the carbon atoms of a molecular chain do not all lie in one plane in stretched rubber. This is the only conclusion which can be drawn from a comparison of the measured fiber axis length of 8.15 Å. and the calculated length of 9.3 Å. of the two isoprene groups (marked with dotted lines in Fig. 2) which constitute the repeating unit in the molecular chain of rubber. The value 9.3 is based on the structural formula shown in the figure with the single bond length 1.54 Å.; the double bond, 1.38 Å.; the single bonds oriented at tetrahedral angles in space; and the double bond along the bisector of the angle between the positions of the two single bonds which it replaces. (That is, the angle ϕ in Fig. 2 has the value 109.5° , not 120° . This choice is best supported by modern conceptions.⁷)

Without violating these restrictions on bond lengths and angles the molecule may have a different configuration if sections of it are moved by rotations about the single bonds joining them to adjacent sections. A careful study of the distances between atoms in the plane configura-

(6) In *J. Research Nat. Bur. Standards*, **19**, 479 (1937), Clark, Wolthuis and Smith report measurements which confirm the absolute values of planar spacings found by Lotmar and Meyer. Our attention was given more to relative than to absolute values. With their figures and the angle $\alpha = 109.5^\circ$, the calculated density is about 0.965, agreeing exactly with what they refer to as "the highest measured value to be found in the literature."

(7) See the work of Brockway and others. A summary and an extensive bibliography are given in *Rev. Modern Phys.*, **8**, 231 (1936).

tion hints that there must be such rotations to avoid the very short interatomic distances which that arrangement involves. For if anything like "free" rotation can occur on single bonds, rotation on bond *a* (Fig. 2) should give carbons one and two almost the relative freedom of atoms belonging to different molecules. Consequently, these carbons and their associated hydrogens should not approach markedly closer than similar groups belonging to different molecules in the crystals of other compounds. In the crystals of ethane, hexamethylbenzene, and hexamethylenetetramine the closest approach of carbons belonging to different molecules has been found to be, respectively, 3.64, 3.69, and 3.72 Å. Further, in such crystals hydrogen has been observed to have a domain radius of 1.29 Å., or a minimum hydrogen-hydrogen distance of about 2.58 Å. Actually the separation of the carbons marked 1 and 2 in Fig. 2 based on the plane configuration and the above atomic spacings is only 2.6 Å., and that of their associated hydrogens, only 1.8 Å. The comparison shows that such short distances between unbonded atoms are very unlikely to occur. This appears to be sufficient explanation of the non-existence of the plane arrangement.

Thus we conclude that even in stretched rubber the angular positions around the single bonds are not those of the planar arrangement, because of the tremendous repulsions which would be involved. Other authors have pointed out that rotations about the single bonds are almost certainly the changes which take place in the molecule during stretching and retraction. Surely then, as these rotations occur during stretching, they are opposed, at least toward the limit of stretch, by the repulsions which prevent the molecule from assuming the plane form. Probably these repulsions predominate over the whole range of stretch, because the prevailing hydrogen-hydrogen distances in the closest pairs, which will have the most effect, also suggest that the forces are more likely to be repulsive than attractive. Then the end-point of stretch of a molecule is reached when the repulsions just balance the externally applied stress; and the end-point of

retraction is the point at which they are balanced by other interatomic forces. This suggestion is at variance with the ideas of Mack,⁸ who envisions hydrogen-hydrogen attractions opposing stretch and returning the molecule to its "retracted" shape after the release of stress.

This picture of predominantly repulsive forces increasing as the molecule approaches its configuration in stretched rubber is particularly attractive, because it is consistent with forces of increasing strength near the end-point and is, therefore, a most plausible explanation of the increasing steepness of the outer part of the stress-strain curve.

The kind assistance of Professors J. C. Slater and B. E. Warren is acknowledged with thanks.

Summary

With the more extensive data from new X-ray films of the diffraction pattern of stretched rubber made in a cylindrical camera, an attempt has been made to find the true unit cell. No really satisfactory solution has been reached. The leading possibilities are described. They are characterized by a change of the angle between the two independent sets of planes which reflect the two strong equatorial spots from 90°, the value which first suggests itself, to 109.5°. The new choice is shown to be consistent with all the evidence. It has the great advantage of resolving fairly well the familiar discrepancy between measured and calculated values of the density of the crystals in stretched rubber. The new value from the unit cell is 1.00.

A necessary consequence of the X-ray data is that the carbon atoms of a molecular chain are not coplanar in stretched rubber. The reason appears to be the large repulsive forces which would have to exist in that configuration. In rotations on the single bonds during stretching and retraction the interatomic forces are probably repulsions in the dominating pairs. Repulsions give a plausible explanation of the form of the outer part of the stress-strain curve.

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(8) Mack, *THIS JOURNAL*, 56, 2757 (1934).