Oxidation of a Sprucewood Glucomannan with Lead Tetraacetate[1]

JOHN M. VAUGHAN[2] AND E. E. DICKEY

The Institute of Paper Chemistry, Appleton, Wisconsin

Received August 19, 1963

A glucomannan obtained from white spruce, *Picea glauca* (Moench) Voss., was oxidized with lead tetraacetate in 80% aqueous acetic acid. The D-mannose–D-glucose ratio dropped from 3.25 to 1.5 and was stable to further oxidation in the same medium. The stability was ascribed to the possible formation of acetals between the aldehyde groups, produced in the oxidation, and the secondary hydroxyl groups on adjacent mannose units. Selective hydrolysis of the oxidized glucomannan produced D-mannose, D-glucose, 4-*O*-β-D-glucopyranosyl-D-mannose, and cellobiose.

The most abundant hemicellulosic components of coniferous woods are the glucomannans which represent 10–15% of the weight of the wood.[3,4] These polysaccharides are linear heteropolymers,[3–9] composed mainly of β-D-mannopyranose and β-D-glucopyranose units linked glycosidically at position 4 in the proportion of approximately 3:1, and with degrees of polymerization <200. Frequently, small amounts of D-galactose are combined with the glucomannans. However, these polysaccharides are distinct from the galactoglucomannans also found in softwoods.[3] Recently, the acetyl content of coniferous wood was located as acetate ester groups on some of the secondary hydroxyl groups along the glucomannan chains.[5]

Although the sequence of sugar residues within the polymer molecules was known to be more or less random, as indicated by the oligosaccharides identified in the products of partial hydrolysis of glucomannans,[7–9] the proportion of adjacent glucose linkages had not been determined. In an attempt to elucidate further the structure of these polymers with respect to such linkages, a method was selected by which most of the mannose units were destroyed with lead tetraacetate[10,11] while any glucose-to-glucose segments were preserved. The general method has been used to study the selectivity of lead tetraacetate toward the mannose units in wood pulps.[12–14]

The starting material was a purified glucomannan (free of ester groups) which was prepared from white spruce, *Picea glauca* (Moench) Voss., according to a procedure described elsewhere.[15]

Attempts to oxidize suspensions of the dried polymer with lead tetraacetate dissolved in aqueous acetic acid were unsuccessful. However, the addition of a dispersion of the polymer in aqueous sodium hydroxide to a solution of lead tetraacetate dissolved in glacial acetic acid[11,16] resulted in rapid and uniform oxidation. The rates of oxidation were favored by the amount of water in the reaction medium, as shown in Fig. 1, and varied with the concentration of reactants, Fig. 2. For all oxidations in 80% acetic acid the mannose–glucose ratio dropped rapidly from 3.25 to 1.5 and remained essentially constant with time as shown in Fig. 3. When the oxidized polymer was recovered and then subjected to a second oxidation, insignificant amounts of lead tetraacetate were consumed and the mannose–glucose ratio was unchanged. However, when the oxidized polymer was reduced with sodium borohydride,[3,17] the polymer then consumed more oxidant, and the mannose–glucose ratio dropped to *ca.* 1.

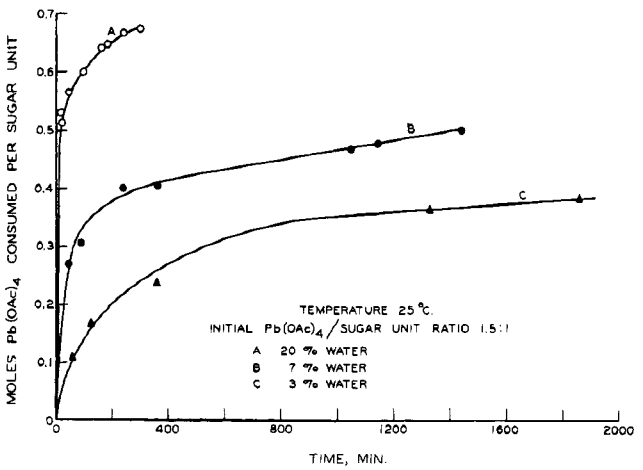


Fig. 1.—Effect of concentration of water on the consumption of lead tetraacetate by the glucomannan.

The stabilization of the partially oxidized glucomannan is believed to be due to the reaction of the aldehyde groups, formed at carbons 2 and 3 of the mannose units, with secondary hydroxyls of adjacent mannose units to form cyclic acetals,[18] as shown schematically in Fig. 4. Apparently, these linkages are sufficiently stable in aqueous acetic acid to block the remaining mannose units toward oxidation.[16,19]

The oxidized polymer was hydrolyzed in dilute aqueous sulfurous acid by the general procedure of Moyer and Isbell.[20] The hydrolysates were analyzed by paper chromatography, and the results, shown in Table I, indicated that cleavage of the oxidized units was

(1) A portion of a thesis submitted by J. M. Vaughan in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence College, Appleton, Wis., June, 1963.

(2) Inland Container Corp., Rome, Ga.

(3) J. K. Hamilton and N. S. Thompson, *Pulp Paper Mag. Can.*, **59**, 233 (1958).

(4) C. T. Bishop and F. P. Cooper, *Can. J. Chem.*, **38**, 793 (1960).

(5) H. Meier, *Acta Chem. Scand.*, **14**, 749 (1960).

(6) A. Tyminski and T. E. Timell, *J. Am. Chem. Soc.*, **82**, 2823 (1960).

(7) M. O. Gyaw and T. E. Timell, *Can. J. Chem.*, **38**, 1957 (1960).

(8) T. E. Timell, *Tappi*, **45**, 734 (1962).

(9) O. Perila and C. T. Bishop, *Can. J. Chem.*, **39**, 815 (1961).

(10) A. S. Perlin, *Advan. Carbohydrate Chem.*, **14**, 9 (1959).

(11) A. S. Perlin and A. R. Lansdown, *Can. J. Chem.*, **34**, 451 (1956).

(12) H. W. Steinmann and B. B. White, *Tappi*, **37**, 225 (1954); A. Roudier and D. Nick, *Mem. Serv. Chim. Etat.* (Paris), **41**, 181 (1957).

(13) K. Matsuzaki and K. Ward, Jr., *Tappi*, **42**, 516 (1959).

(14) R. W. Detrick, *ibid.*, **43**, 634 (1960).

(15) J. M. Vaughan and E. E. Dickey, *ibid.*, in press.

(16) E. Baer, J. M. Grosheintz, and H. O. L. Fischer, *J. Am. Chem. Soc.*, **61**, 2607 (1939).

(17) M. Abdel-Akher, J. K. Hamilton, R. Montgomery, and F. Smith, *ibid.*, **74**, 4970 (1952); J. K. Hamilton and F. Smith, *ibid.*, **78**, 5907 (1956).

(18) V. C. Barry and P. W. D. Mitchell, *J. Chem. Soc.*, 4020 (1954); R. D. Guthrie, *Advan. Carbohydrate Chem.*, **16**, 105 (1961).

(19) A. S. Perlin, *Anal. Chem.*, **27**, 396 (1955).

(20) J. D. Moyer and H. S. Isbell, *Anal. Chem.*, **29**, 1862 (1957).

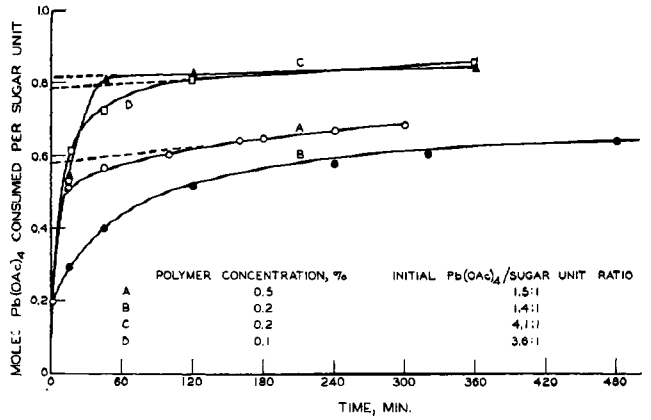


Fig. 2.—Effect of polymer concentration and initial molar ratio of oxidant to sugar unit on the consumption of lead tetraacetate by the glucomannan in 80% acetic acid at 25°.

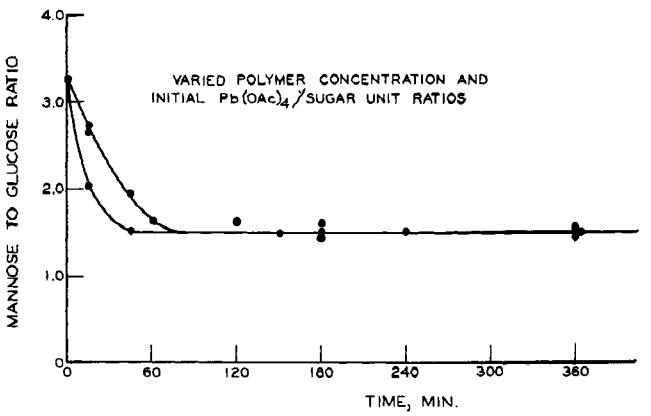


Fig. 3.—Decrease in mannose–glucose ratio in the glucomannan with oxidation time in 80% acetic acid at 25°.

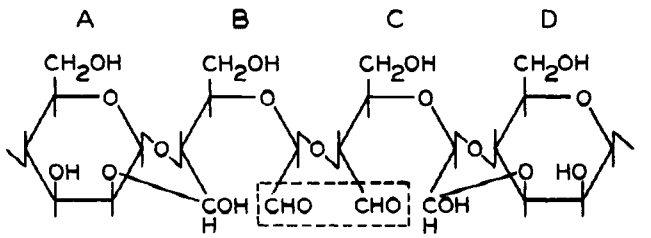


Fig. 4.—Segment (diagrammatic) of a glucomannan after oxidation with lead tetraacetate. (The free aldehydes shown in the dashed box represent the function only, not the true structure.)

accomplished readily and that intact oligosaccharide units were not affected seriously.

As shown in Table II, essentially all of the glucose units present in the oxidized polymer were accounted for in the products of selective hydrolysis, but the recovery of mannose was approximately 60%. The absence of galactose is in accord with its probable location as a branch on the glucomannan chain; in this position it would be oxidized by lead tetraacetate.[21]

By means of preparative chromatography on a cellulose column and on heavy paper, 4-*O*-β-D-glucopyranosyl-D-mannose and cellobiose were isolated from sulfurous acid hydrolysates (Table II). Mannopyranosyl-D-glucose was probably present, but in amounts too small for identification. It is noteworthy that mannobiose and other oligosaccharides were not detected.

(21) Constance M. Ewald and A. S. Perlin, *Can. J. Chem.*, **37**, 1254 (1959).

TABLE I

PAPER CHROMATOGRAPHY OF SULFUROUS ACID HYDROLYSATE OF THE OXIDIZED GLUCOMANNAN AND OF KNOWN REFERENCE COMPOUNDS

Unknown spots	Solvent A R_f[a]	Solvent A R_c[b]	Solvent C R_c[b]
A (Light) glyoxal (?)	0.79		
B (Light) erythrose (?)	0.60		
M (Heavy) mannose	0.23		
G (Heavy) glucose	0.18		
C (Light)		3.00	2.98
D (Medium) 4-*O*-β-D-glucopyranosyl-D-mannose		1.85	1.54
E (Medium) cellobiose		1.00	1.00
F (Faint)		0.58	0.66
Heavy streak		0–0.6	0–0.8
Known spots			
Glyoxal	0.7–0.9		
Erythrose	0.65		
Mannose	0.23		
Glucose	0.18		
4-*O*-β-D-Glucopyranosyl-D-mannose		1.90	1.42
Mannobiose (4-*O*-β-D-mannopyranosyl-D-mannose)		1.05	1.21
Cellobiose		1.00	1.00
4-*O*-β-D-Mannopyranosyl-D-glucose		0.57	0.85

[a] Chromatographic mobility of spot with respect to solvent front. [b] Chromatographic mobility of spot with respect to authentic cellobiose.

TABLE II

COMPOSITION OF GLUCOMANNAN HYDROLYSATES

Anhydrosugar unit	Unoxidized glucomannan: Total hydrolysis in sulfuric acid %	Unoxidized glucomannan: Total hydrolysis in sulfuric acid Mole ratio	Oxidized glucomannan: Total hydrolysis in sulfuric acid %	Oxidized glucomannan: Total hydrolysis in sulfuric acid Mole ratio	Oxidized glucomannan: Selective hydrolysis in sulfurous acid, %
D-Mannose, %	74.4[a]	3.25	24.4[b]	1.48	14.5
D-Glucose, %	22.9	1.0	16.5	1.0	13.5
D-Galactose, %	1.2	0.05	Nil		Nil
Cellobiose, %					1.8 (2.5)[c]
4-*O*-β-D-Glucopyranosyl-D-mannose, %					1.0 (1.6)[c]
4-*O*-β-D-Mannopyranosyl-D-glucose, %					Trace
4-*O*-β-D-Mannopyranosyl-D-mannose, %					Trace (?)

[a] Per cents based on original glucomannan. [b] Per cents based on oxidized polymer. [c] Figures in parentheses are the estimated total amount in the hydrolysate.

The random distribution of cellobiose and cellotriose units in a glucomannan having a mannose–glucose ratio of 3.25 was calculated to be 5.1% and 1.8%, respectively.[22] In contrast, the recovery of 2.5% of cellobiose from the products of selective hydrolysis and the absence of cellotriose indicated that the sequence of mannose and glucose along the polymer chain may not be strictly random.

Otherwise, the results of the oxidation of the glucomannan with lead tetraacetate and of the subsequent hydrolysis of the oxidized polymer were consistent with its linear character.

Experimental

Paper Chromatography.—Schleicher and Schuell No. 598 paper was used unless noted otherwise. All papers used for quantita-

(22) D. L. Taylor, private communication.

tive estimations were dipped in distilled water and dried without tension prior to use. The papers were irrigated with one of three solvents: A, ethyl acetate–pyridine–water (8:2:1); B, butyl acetate–pyridine–95% ethanol–water (8:2:2:1); and C, ethyl acetate–acetic acid–water (9:2:2). The sugars were located by dipping the papers in a solution of 0.5% aniline and 1.5% monochloroacetic acid in anhydrous ether and heating[23] for 5–8 min. at 100°. This reagent was sensitive to 1 μg. of monosaccharide and 2 μg. of disaccharide.

Quantitative Sugar Analysis.—For quantitative analysis of monosaccharides the general method of Saeman and co-workers[24] was used. Disaccharides were determined gravimetrically. Mannose–glucose ratios in the hydrolysates of oxidized samples were determined by a modification of the rapid photometric method of Jeffery, Partlow, and Polglase.[23] The modification involved plotting the ratio of the Kubelka-Munk K/S values for the two sugars *vs.* the ratio of the sugars in solution. The standard deviation about the regression line was 0.1, and the regression was independent of sugar concentration within the limits of spot concentration, 20 to 120 μg.

Measurements of the reflectance of the sugar spots on the chromatogram were simplified by the use of a Welsh Densichron in line of the Model B Beckman spectrophotometer.[23]

Oxidation.—All oxidations were made in aqueous acetic acid at 25°. Lead tetraacetate as a saturated solution in glacial acetic acid was analyzed before use according to the potassium iodide–sodium thiosulfate technique described by Detrick.[14] In a typical oxidation, 10 g. of glucomannan was dissolved in 100 ml. of 7 N sodium hydroxide and the solution was diluted with 287 ml. of water. Lead tetraacetate stock solution (1300 ml.) in a 3-l., round-bottomed flask was diluted with 340 ml. of glacial acetic acid. The reaction was initiated by pouring the alkaline solution of the glucomannan into the acetic acid solution with vigorous stirring. Thus, the reaction mixture was composed of 0.5% by weight of glucomannan dispersed in 80% aqueous acetic acid containing 1.5 moles of lead tetraacetate per sugar unit. An oxidation blank was prepared by the same procedure and run concurrently with each oxidation sample.

The course of the reaction was followed by removing aliquots from the reaction flask at selected time intervals and by determining the consumption of oxidant.

At the end of the reaction, the precipitate of oxidized glucomannan was separated by filtration and washed with 50% aqueous acetic acid. The filtrate and washings were combined, and the remaining lead tetraacetate was destroyed by the addition of aqueous oxalic acid. Precipitated lead oxalate was separated by filtration and washed with water.

The material which had precipitated during the reaction was dissolved in water and combined with the filtrate, and the clear solution was concentrated under vacuum on a rotary evaporator until the solution became turbid. The solution was then diluted with 10 volumes of absolute ethanol to precipitate the oxidized glucomannan. The precipitate was recovered by centrifugation, washed with absolute alcohol and anhydrous ether, and dried at reduced pressure at room temperature. The oxidized glucomannan was redissolved in water and passed through an ion-exchange column containing Amberlite[25] IR-120 to remove inorganic cations. The effluent was concentrated to a thin sirup under vacuum, and the product was recovered by freeze-drying; the yield was 65.5%.

Two-Stage Oxidations. A.—The oxidized glucomannan was recovered from the initial oxidation solution, washed with glacial acetic acid, and treated with fresh oxidant in a second step. No additional oxidation was noted, and the mannose–glucose ratio remained unchanged.

B.—The oxidized glucomannan was reduced with sodium borohydride by the procedure of Bishop and Cooper[4] and subjected to a second oxidation step. Additional lead tetraacetate was consumed, and the mannose–glucose ratio was diminished from 1.5 to 1.2 in one experiment and to 0.7 in another; yields of oxidized products were only 7.5% of the glucomannan.

Selective Degradation of the Oxidized Polymers.—Sulfurous acid was prepared by saturating distilled water with sulfur dioxide at 25°. Saturated sulfurous acid (100 ml.) and 2.0 g. of oxidized glucomannan were placed in a 200-ml. round-bottomed glass pressure vessel. The polymer dissolved rapidly, forming a pale yellow solution. The vessel was tightly capped and placed in an oil bath at 100° for 3.5 hr. After hydrolysis most of the sulfur dioxide was removed under vacuum, sulfite and sulfate ions were removed by precipitation with barium hydroxide, and excess barium was removed with sulfuric acid. The clear solution was concentrated to 10 ml. on a rotary evaporator, benzoic acid (10 mg.) was added as a preservative, and the sirup was stored at 0° until used.

Separation of Hydrolysis Products.—Qualitative identification of the hydrolysis products was made by paper chromatography with known oligosaccharides in solvents A and C.

Glucose and mannose in the hydrolysate were determined spectrophotometrically by the general procedure of Saeman and co-workers.[24]

The disaccharides were separated on a 5 × 55 cm. column of Whatman cellulose powder. The entire hydrolyzate was adsorbed on 5 g. of cellulose powder suspended in solvent A, the slurry was poured onto the column with a minimum of solvent, and the solids were allowed to settle into a uniform layer. The monosaccharides were eluted with solvent A, and the disaccharides were eluted by changing the solvent ratio of ethyl acetate–pyridine–water to 6:3:3. The yields and composition of the several fractions are summarized in Table III.

TABLE III

CELLULOSE COLUMN CHROMATOGRAPHY OF SULFUROUS ACID HYDROLYSATE OF THE OXIDIZED GLUCOMANNAN

Fraction	Weight, g.	Qualitative identification by paper chromatography
1	0.0545	Unknown C
2	0.0522	Mixture of unknown C and 4-*O*-β-D-glucopyranosyl-D-mannose
3	0.1048	4-*O*-β-D-glucopyranosyl-D-mannose
4	0.0815	Mixture of 4-*O*-β-D-glucopyranosyl-D-mannose and cellobiose
5	0.1188	Cellobiose
6	0.1123	Trace cellobiose
7	0.7495	Heavy streak

Investigation of Fractions.—Fraction 3 was placed on a 22 × 24 in. Whatman No. 3 MM sheet in three 5-in. streaks separated by half-inch guide spots. The chromatogram was eluted with solvent A for 48 hr. After elution, the carrier strips were cut from the sheet, and the guide spots were developed with aniline–monochloroacetic acid developer. The portions of the carrier strips which contained the disaccharide, chromatographically identical with 4-*O*-β-D-glucopyranosyl-D-mannose, were cut out and eluted with water. The purified disaccharide was recovered as a tan sirup in a 0.0202-g. yield, $[\alpha]^{23}D$ +9.8° (*c* 1.01, water); hydrolysis produced mannose and glucose in the ratio of 1:1. Unfortunately, attempts to crystallize the disaccharide were unsuccessful. The octaacetate was prepared and was crystallized from 95% ethanol with m.p.[26] 198–200°; upon admixture with octa-*O*-acetyl-4-*O*-β-D-glucopyranosyl-α-D-mannose (m.p. 199–200°), the melting point was unchanged. The infrared spectra of the two acetates were identical.

Fraction 5 was resolved into three subfractions by large-scale paper chromatography as above. Subfraction 5-1 contained mostly colored impurities and yielded 0.0177 g. The principal spot had an R_c of 0.6 in solvent A and 0.74 in solvent C. Hydrolysis of the subfraction afforded chromatographic spots for mannose and glucose in approximately equal amounts.

Subfraction 5-2 was isolated from the leading edge of the major component of fraction 5 and yielded 0.0120 g. Chromatographic analysis of this material showed that it had an R_c of 1.0 in solvent A and an elongated R_c of 1.0–1.1 in solvent C. The leading edge of the elongated spot moved slightly more slowly than mannobiose in solvent C. Hydrolysis of this subfraction afforded mostly glucose. A small amount of mannose also was found.

(23) J. E. Jeffery, E. V. Partlow, and W. J. Polglase, *Anal. Chem.*, **32**, 1774 (1960).

(24) J. F. Saeman, W. E. Moore, R. L. Mitchell, and M. A. Millett, *Tappi*, **37**, 336 (1954).

(25) Ion-exchange resin manufactured by Rohm and Haas, Philadelphia, Pa.

(26) Melting points are uncorrected.

The largest subfraction 5-3, chromatographically identical with cellobiose, was concentrated to an amber sirup, yielding 0.0265 g., $[\alpha]^{23}D$ +30.8° (*c* 0.88, water); hydrolysis produced glucose only. Crystalline material formed in aqueous acetic acid was removed by filtration, washed with acetone, and dried under vacuum and had m.p. 231–233°, unchanged upon admixture with authentic cellobiose. The infrared spectrum of the crystals was identical with that of authentic cellobiose.

Dissociation Constants of the Cyanohydrins of Some Methyl-Substituted Cyclobutanones, Cyclopentanones, and Cycloheptanones. Conformation of These Rings

OWEN H. WHEELER AND ELSIE GRANELL DE RODRIGUEZ

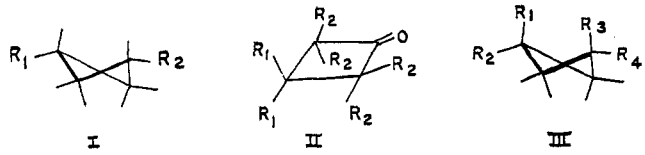
The Department of Chemistry and The Puerto Rico Nuclear Center,[1] University of Puerto Rico at Mayaguez College Station, Mayaguez, Puerto Rico

Received October 31, 1963

The dissociation constants of the cyanohydrins of a number of methyl-substituted cyclobutanones, cyclopentanones, and cycloheptanones have been determined in 95% ethanol at 23°. The results suggest that the cyclobutanone ring is slightly puckered, that cyclopentanone exists in a flexible half-chair or envelope conformation, and that the cycloheptanone ring is a flexible chair.

A study of the dissociation constants of the cyanohydrins of methyl-substituted cyclohexanones[2] has shown the large steric effect of this substituent in an axial position. The present study concerns ketones of smaller and larger rings, and the results are discussed in relation to the conformation of these rings.

Cyclobutanone.—A number of spectroscopic and thermodynamic studies of cyclobutane[3] have shown that the ring is puckered (I). A recent study[4] of the



I II III

isomeric methyl 3-methylcyclobutanecarboxylates has shown that the *cis* isomer (I, $R_1 = CH_3$; $R_2 = CO_2CH_3$) is more stable, and this is only consistent with a puckered ring conformation. The conformation of cyclobutanone is less certain. Its high infrared carbonyl stretching frequency[5] has been interpreted[5b] in terms of a "slightly puckered" ring with an internal ring carbonyl angle of only 82 ± 9°. Recent measurements[4] of the dipole moment, and ultraviolet and infrared spectra of α-bromocyclobutanone show that it exists largely with the carbon–bromine bond "axial" at an angle of 101° to the carbonyl dipole (*i.e.*, a near planar ring), although in polar solvents, this bond is partially "equatorial" (*i.e.*, a puckered ring as in I).

The value of the dissociation constant of cyclobutanone cyanohydrin (see Table I) determined in the present work is in good agreement with a previous value (0.84×10^{-2}) determined using carefully purified ketone,[6a] but is smaller than the value (4.5×10^{-2}) reported by Ruzicka and co-workers.[6b] The two substituted cyclobutanones had cyanohydrin dissociation constants larger than the unsubstituted ketone, although the differences are smaller than for similarly substituted cyclohexanones.[2]

TABLE I

DISSOCIATION CONSTANTS OF CYANOHYDRINS[a]

	$K_D \times 10^2$
Cyclobutanone	0.922
3,3-Dimethyl-	21.2
2,2,4,4-Tetramethyl-	2.72
Cyclopentanone	2.98[b]
2-Methyl-	3.15
3-Methyl-	3.71
2,4-Dimethyl-	3.90
2,5-Dimethyl-	4.71
2,2,4-Trimethyl-	1.92
2,4,4-Trimethyl-	6.71
2,2,4,4-Tetramethyl-	19.0
Cyclohexanone	0.059[c]
Spiro[4.4]nonan-1-one (XIII)	12.3
Spiro[4.5]decan-6-one (XIV)	1.57
Cycloheptanone	8.77[d]
2-Methyl-	17.8
3-Methyl-	8.56
4-Methyl-	10.8
3,3,5-Trimethyl-	25.3
3,5,5-Trimethyl-	10.3
3,3,5,5-Tetramethyl-	28.4

[a] In 95% ethanol at 23 ± 1°. [b] Ref. 2 gives 2.05 at 25°. [c] From ref. 2. [d] A. Lapworth and R. H. F. Manske [*J. Chem. Soc.*, 2533 (1923)] give $K_D \times 10^2 = 7.96$ at 20°, and V. Prelog and M. Kobelt [*Helv. Chim. Acta*, **32**, 1187 (1949)] give 13 at 22–23°.

The two opposing factors of ring angle strain and nonbonded hydrogen interactions[2] are responsible for the nonplanar conformation of cyclobutane. In cyclobutanone the ring angle strain is considerably increased and any departure from a planar conformation will increase angle strain. However, the nonbonded hydrogen interactions are reduced from eight in a planar conformation of cyclobutane to only four in cyclobutanone. Although I-strain is relieved on forming the

(1) The Puerto Rico Nuclear Center is operated by the University of Puerto Rico for the Atomic Energy Commission under Contract No. AT-(40-1)-1833.

(2) O. H. Wheeler and J. Z. Zabicky, *Chem. Ind.* (London), 1388 (1956); *Can. J. Chem.*, **36**, 656 (1958).

(3) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952); G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5634 (1953); A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961).

(4) J. M. Conia, J. L. Ripoll, L. A. Tushans, C. L. Neumann, and N. L. Allinger, *J. Am. Chem. Soc.*, **84**, 4983 (1962).

(5) (a) K. Frei and H. H. Gunthard, *Helv. Chim. Acta*, **43**, 649 (1960); (b) R. Zbinden and H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1215 (1960).

(6) (a) H. C. Brown and O. H. Wheeler, in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 238; (b) L. Ruzicka, P. A. Plattner, and H. Wild, *Helv. Chim. Acta*, **28**, 613 (1945).