1 g. of zinc dust. The solution was then steam distilled and the distillate neutralized with calcium carbonate and concentrated to give 0.775 g. of a white calcium salt, $[\alpha]^{25}D$ +0.7° (*c* 1.4, water). A solution of 0.421 g. of the calcium salt in 30 ml. of water was stirred with Amberlite IR-120(H) resin to give a solution of the free acid, $[\alpha]^{25}D$ +1.8° (*c* 1.1, water), which was neutralized with sodium hydroxide to give 0.404 g. of the sodium salt.

When 0.195 g. of the sodium salt was dissolved in 1 ml. of water and refluxed for 1 hr. with 0.5 g. of *p*-bromophenacyl bromide in 5 ml. of alcohol, crystals of the *p*-bromophenacyl ester separated. After one recrystallization from ethanol, the ester had m.p. 52–53°, undepressed on admixture with the *p*-bromophenacyl ester of α-methylbutyric acid.

Anal. Calcd. for $C_{13}H_{15}O_3Br$: C, 52.17; H, 5.06. Found: C, 52.01; H, 5.03.

The *p*-phenylphenacyl ester was similarly prepared. Recrystallized once from ethanol, the crystals had m.p. 68–68.5°, undepressed on admixture with the *p*-phenylphenacyl ester of α-methylbutyric acid.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT DEPARTMENT, U. S. NAVAL POWDER FACTORY]

Spectrophotometric Studies on the Action of Sulfuric Acid on Reducing Sugars and the Isolation and Identification of the Ether-soluble Substances Produced from Pentoses under Acid Conditions[1]

BY F. A. H. RICE AND LAWRENCE FISHBEIN

RECEIVED AUGUST 29, 1955

Ultraviolet spectrophotometric studies on reducing sugars in solutions of sulfuric acid–water over a wide range of temperature and acid concentration indicate no differences in the reaction products formed from individual sugars in the same series. Observed differences in the ultraviolet absorption spectra of a series of hexoses or pentoses at the end of a specified interval of time are attributable to the difference in the rate of development of both the absorption maxima and the final apparent equilibrium reached by the individual sugars. In the pentose series under all conditions investigated, the relative rates of development of the ultraviolet absorption and apparent final maxima were: D-lyxose > D-ribose > D-xylose > D-arabinose. The rates at which compounds having absorption in the ultraviolet region were formed from a sugar increased with both increased acid concentration and increased temperature. The compounds responsible for the characteristic ultraviolet absorption curve of a reducing sugar in sulfuric acid solution are ether soluble. However, weak absorption observed between 220 and 260 mμ after ether extraction suggests that small amounts of unsaturated compounds remain in the aqueous phase. Examination of the ether extract has shown that not only is furfuraldehyde formed in the reaction of a pentose with aqueous H_2SO_4, but acetaldehyde, formaldehyde and crotonaldehyde are produced as well. The aldehydes were separated and identified as their 2,4-dinitrophenylhydrazones. Separation was accomplished by means of chromatography on silicic acid.

When reducing sugars are dissolved in acid solution at room temperatures or lower (6–10°), the observed optical rotations are found to increase[2] as the concentration of acid is increased,[3] and although the monosaccharide can be recovered in almost quantitative yield,[2] a certain proportion condenses to form disaccharides.[4] It is possible that an equilibrium reaction is involved.[3] The increase in observed optical rotation is probably due to an increase in the concentration of the *aldehydo* form of the sugar.[5]

Both *anhydro* sugars[6] and disaccharides[7] are formed when a reducing sugar is treated with hot, dilute (0.2–0.5 *N*) mineral acids.

Heat and moderately concentrated mineral acids (2–5 *N*) lead to extensive degradation of the sugar molecule. Hexoses yield 5-(hydroxymethyl)-2-furaldehyde,[8] while the pentoses produce furfuraldehyde.[9] Quantitative yields, however, are obtained only under specific conditions[10] of temperature and acid concentration.

It is possible that mineral acid is not essential for the transformation hexose → 5-(hydroxymethyl)-2-furaldehyde[11] or pentose → furfuraldehyde. Haworth and Jones[12] found that while D-fructose formed considerable quantities of 5-(hydroxymethyl)-2-furaldehyde when treated with a hot oxalic acid solution, D-glucose was recovered unchanged. That limited quantities of 5-(hydroxymethyl)-2-furaldehyde are formed at *p*H 6.5 has been shown definitely by the ultraviolet studies of Wolfrom, Schuetz and Cavalieri.[13] The effect of *p*H in relation to the browning reaction has been studied by Kroner and Kothe[14] who found the rate of degradation to have only slight dependence on *p*H above 3.

Spectrophotometric studies of the behavior of carbohydrates in 79% (weight/volume) sulfuric acid[15] show that after 2 hours at 25° or 15 minutes at 100°, each of the series of hexoses studied had a characteristic ultraviolet absorption curve, which was similar, but not superimposable, upon the curve of 5-(hydroxymethyl)-2-furaldehyde. Bandow[16] also found that a pentose after one day in

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[1] Published with permission of the Bureau of Ordnance, Navy Department. The opinions and conclusions are those of the authors.

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[14] W. Kroner and H. Kothe, *Ind. Eng. Chem.*, **31**, 248 (1939).

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concentrated acid gave an ultraviolet absorption curve that was similar to, but not superimposable upon, that of furfuraldehyde. Love[17] has interpreted the ultraviolet absorption curves obtained on a series of hexoses and pentoses in 28.3 N sulfuric acid to indicate that four compounds with characteristic ultraviolet absorption spectra are formed when reducing sugars are treated with concentrated acids.

Since any disaccharides or *anhydro* sugars formed under acid conditions would not contribute to the observed ultraviolet absorption, and the production of furfuraldehyde from pentoses or 5-(hydroxymethyl)-2-furaldehyde from hexoses does not completely account for the ultraviolet absorption, other hitherto unrecognized compounds must be produced. As a preliminary step in an investigation of the compounds responsible for the ultraviolet absorption, the effect of acid concentration, temperature, and time on the development of the ultraviolet absorption was investigated.

In addition we wish to report the separation and identification of the ether-soluble reducing substances produced when a pentose is treated at room temperature with sulfuric acid.

Results and Discussion

The influence of acid concentration, temperature, time and stereochemical configuration on the development of ultraviolet absorption of a reducing sugar in acid solution was studied over acid concentrations ranging from 1 to 20 N at room temperatures (approx. 25°) and at the temperature of the boiling water-bath (hereafter referred to as 100°). The ultraviolet absorption spectrum was measured at 0.25 to 0.5-hour intervals over a period of five hours. The D-series of pentoses, D-glucose, D-galactose, D-mannose and L-arabinose were examined.

In accord with the results of other workers,[15,17] it was found that each of the reducing sugars gave a characteristic ultraviolet absorption curve when the sugars were heated under the same conditions for the same length of time. When comparisons were made of the ultraviolet absorption curves obtained at intervals over a period of 4 hours it was apparent that the shape of the absorption curve was the same for each of the pentoses and, although the curves obtained from the hexoses differed from those of the pentoses, the hexoses showed the same similarity to each other. This result would be expected if a single substance or a mixture of substances in constant ratio were being formed from the pentose as it is heated in acid solution. Each pentose showed the same ultraviolet absorption spectrum. For example, when D-lyxose and D-xylose were heated at 100° in 8.2 N H_2SO_4 for 60 and 120 minutes, respectively, their ultraviolet spectra were almost superimposable.

It should be noted that while the ultraviolet curve approximates that of furfuraldehyde, the relative heights of the absorption maxima[18] indicate the presence of other substances. That the compounds produced and their relative concentrations are the same for each pentose is strongly suggested by the fact that the ratio of the heights of the absorption maxima for each pentose is the same, and that the ratio of the absorption maxima does not change appreciably with the time of heating. This is shown in Table I in which the ratios of the optical density (O.D.) at 277 and 227 mμ for the D-pentose series are given. The sugars were heated at 100° in 8.2 N H_2SO_4 for the indicated times.

TABLE I

RATIO OF ABSORPTION MAXIMA OF THE D-PENTOSES IN 8.2 N H_2SO_4 AT 100°

Time, min.	Ratio O.D.$_{277\ m\mu}$/O.D.$_{228\ m\mu}$ Compound			
	D-Arabinose	D-Xylose	D-Lyxose	D-Ribose
10		2.48	2.43	
20	2.95			2.92
25			2.85	
30	3.05	3.04	2.92	2.95
40	2.95	3.12		2.96
50	2.94	3.05	3.02	2.88
110	2.88	2.90		3.11
240	2.64	2.63		

It was found that the same ultraviolet absorption curves developed at room temperature as at 100°. The rate at which they developed, however, was much slower. The ratio of the absorption maxima was the same at room temperature as at 100°.

Although the initial development of the absorption maxima is quite rapid, a point is reached (in the case of D-arabinose in 8.2 N H_2SO_4 after 180 minutes) at which an apparent equilibrium is reached. This is better shown in Fig. 1, where the absorption maxima at 277 mμ for the four pentoses are plotted as a function of time. It will be seen that the rate at which substances with ultraviolet absorption characteristics were produced and as suggested by the curves the final apparent equilibrium which was reached after 40 hours was also characteristic of the pentose.

Increasing the concentration of H_2SO_4 from 1 to 20 N does not change the shape of the ultraviolet absorption curve or the ratio of the two maxima. It does change, however, the point and rate at which apparent equilibrium is reached. Figure 2 shows the effect of increasing the acid concentration on the rate of development of the absorption maxima at 277 mμ. It should be noted that the vertical axis is on a logarithmic scale in order to depict, on the same graph, the effect of several concentrations of acid. At the point of apparent equilibrium, the pentose still could be isolated. The procedure for isolation will be reported in a later paper.

Almost quantitative yields of furfuraldehyde can be obtained from the pentoses when the furfuraldehyde is removed as it is formed,[10] and even when the furfuraldehyde is not removed, complete destruction of the sugar will occur on prolonged heating. It may be that the equilibrium suggested in Figs. 1 or 2 is one in which the rate of decomposition of the pentose into products with absorption characteristics is balanced by the production of the "humic substances" of unknown composition.

When the hexoses were studied, it was found that

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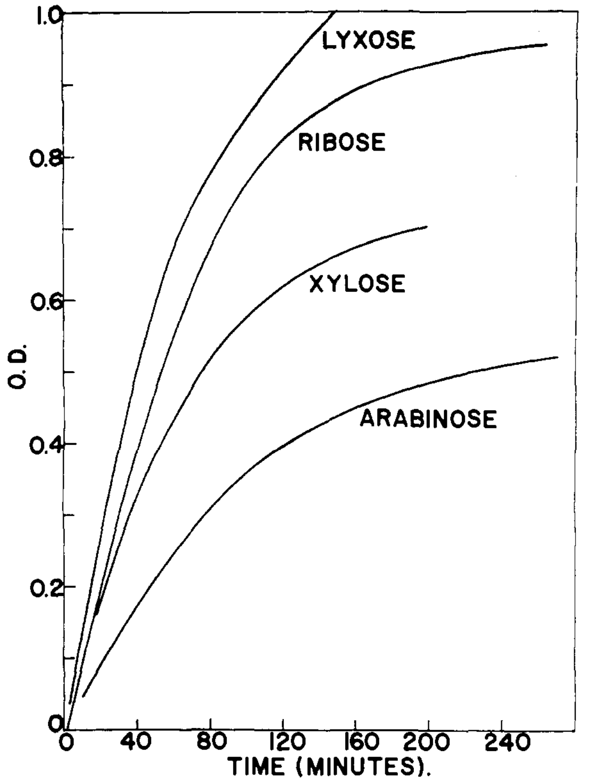

Fig. 1.—Comparison of the rates of development of ultraviolet absorption at 277 mμ for the D-pentoses in 8.2 N H_2SO_4 at 100°; concentration of pentose; 4 mg./100 ml.

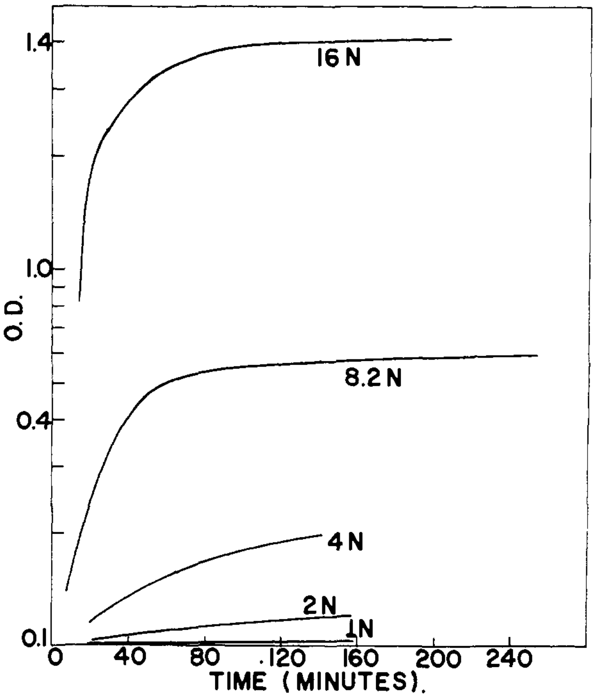

Fig. 2.—Effect of concentration of H_2SO_4 on the development of absorption at 280 mμ: sugar, D-arabinose; temperature, 100°; normality of acid as indicated; concentration, 4 mg./100 ml.

although the curves were similar, the ratio of the absorption maxima, was not constant. The height of the peak at 227 mμ increased more rapidly than the peak at 277 mμ and approached that of the peak at 277 mμ over the period of time studied. The same change occurred with all the hexoses studied, but the rate was characteristic of each. A plot of absorption maxima at 277 mμ against time yielded a set of curves similar to those obtained from the pentoses (Fig. 1).

Since even in the case of the pentoses it is unlikely that the observed ultraviolet absorption spectrum is due to a single substance,[15–17] it was considered of interest to determine whether or not the observed absorption could be separated into absorption due to ether-soluble substances (such as furfuraldehyde) and ether-insoluble substances which might represent intermediates in the formation of the furan compounds from reducing sugars.

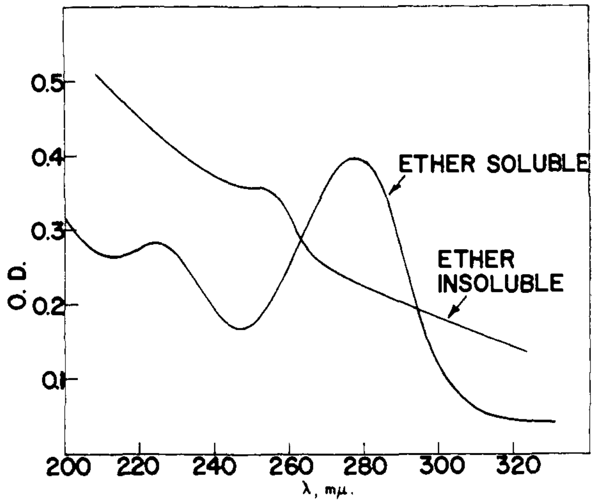

Fig. 3.—Ultraviolet absorption of ether-soluble and ether-insoluble products from xylose in 8.2 N H_2SO_4: concentration of D-xylose, 1 g./100 ml.; time of heating, 3 hours; ether extract (100 ml.) diluted 1:400 (by volume).

Figure 3 shows the ultraviolet absorption curve obtained from the ether extract of D-xylose after it had been treated with 8.2 N H_2SO_4 for 3 hours at 100°. The curve has the same general characteristics as the original sugar. The ratio of the absorption maxima is not the same, however, and this difference is not accounted for by the absorption of the aqueous phase. It should be noted that the ether extract has been diluted 1:400; the ether-insoluble phase was not significantly diluted. The absorption of the aqueous phase between 200 and 280 mμ, therefore, is not great compared to that of the ether-soluble material. That there is absorption, however, suggests the presence of conjugated unsaturated compounds in low concentration.[19] The observed difference in the ratio of the absorption maxima between the ether extract and the acid solution of the pentose may possibly be due to the difference in solvents.[20] It is known that not only the position but the intensity of the absorption maxima depend on the solvent.[21] When D-arabin-

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[20] R. B. Woodward, *ibid.*, **63**, 1123 (1941).

[21] A. Burawoy, *J. Chem. Soc.*, 1177 (1939).

ose, D-ribose and D-lyxose were extracted with ether in the same manner, essentially the same results were obtained.

Isolation and Identification of the Ether-extractable Products.—Since the concentration of the acid affected only the rate at which compounds showing ultraviolet absorption were formed and not so far as could be determined the final products, a concentration of sulfuric acid (20 N) was chosen which would give maximum absorption in 20–48 hours at room temperature. By running the reaction at room temperature the solution could be continuously extracted with ether and thus remove any ether-soluble products as they were formed. In particular, furfuraldehyde, which can be destroyed in acidic media,[22] should be stable under these conditions. Reeves and Munro[23] found that very little if any destruction of furfuraldehyde took place in a mixture of boiling aqueous HCl and xylene. The xylene presumably removed the furfuraldehyde as formed.

The 2,4-dinitrophenylhydrazones of the ether-soluble reducing compounds were formed by shaking the ether extract with Brady reagent[24] (0.3 g. of 2,4-dinitrophenylhydrazine per 100 ml. of 2 N HCl). The mixture of 2,4-dinitrophenylhydrazones was then separated by chromatographing them on silicic acid[25]–Celite.[26] Four colored zones were observed. The zones were eluted with ethanol, crystallized and identified as the 2,4-dinitrophenylhydrazones of furfuraldehyde, formaldehyde, crotonaldehyde and acetaldehyde by their ultraviolet absorption spectra, analyses, melting point and mixed melting point with the corresponding known compound.

It is well known that furfuraldehyde is formed when a pentose is treated with acid[27]; indeed its production is the basis of the various color tests for pentoses.[9] Formaldehyde, acetaldehyde and crotonaldehyde, however, have not, so far as we are aware, been identified as products resulting from the reaction of pentoses with mineral acids. Since formic acid has been found to arise as a result of heating furfuraldehyde with H_2SO_4[28] it is conceivable that the formaldehyde isolated was due to the further degradation of the furfuraldehyde produced. We think this is highly improbable because of the relatively low temperature used. In addition, since formic acid itself will not react with Brady reagent,[29] formaldehyde would need to be produced from furfuraldehyde in place of formic acid. There is no evidence that formaldehyde is produced from furfuraldehyde in acid solution.

When individual pentoses are treated under the same conditions with mineral acids, the amount of furfuraldehyde produced depends on the stereochemistry of the pentose.[9] It is also true that the yield of furfuraldehyde based on the weight of an insoluble derivative is in general much lower than the yield based on the direct titration of the aldehyde group.[9] We should like to suggest that furfuraldehyde, acetaldehyde, formaldehyde and crotonaldehyde are produced concurrently when a pentose is treated with acid and hence quantitative production of furfuraldehyde is impossible. Since the rate at which these compounds are produced depends on the stereochemistry of the pentose, the yield of furfuraldehyde would depend on a number of complex variables related to the rate of production of the aldehydes and their further degradation in acid solution. The low yields based on gravimetric methods are also explained since they depend on the insolubility of a furfuraldehyde derivative which would not necessarily include other aldehydes and hence give lower values than a direct aldehyde titration.

As, after recrystallization, we can account for the identity of 86.5% of the 2,4-dinitrophenylhydrazones prepared from the ether extract and these hydrazones are found in four discrete zones, only very small, if any, amounts of other compounds can be present. The reducing compounds responsible for ultraviolet absorption in the pentose series are therefore furfuraldehyde, acetaldehyde, formaldehyde and crotonaldehyde.

Since the rate at which these compounds are formed depends on the configuration of the pentose, we hope further investigations will assist in elucidating the role stereochemistry plays in the mechanism of sugar reactions.

Experimental

The ultraviolet absorption spectra were taken at room temperature on a Beckman model DU quartz spectrophotometer.

Materials.—The reducing sugars examined had the following constants[30]: D-arabinose, m.p. 158°, $[\alpha]^{22}\mathrm{D}$ $-104°$ (H_2O, *c* 9); D-xylose, m.p. 142–144°, $[\alpha]^{22}\mathrm{D}$ $+19°$ (H_2O, *c* 6); D-lyxose, m.p. 100°, $[\alpha]^{22}\mathrm{D}$ $-15°$ (H_2O, *c* 10); D-ribose, m.p. 94–96°, $[\alpha]^{22}\mathrm{D}$ $-22°$ (H_2O, *c* 4); D-glucose, $[\alpha]^{22}\mathrm{D}$ $+52.2°$ (H_2O, *c* 4); D-galactose, $[\alpha]^{22}\mathrm{D}$ $+80°$ (H_2O, *c* 4); D-mannose $[\alpha]^{22}\mathrm{D}$ $+14°$ (H_2O, *c* 4). These values are in good agreement with those reported in the literature.[31]

Procedure.—The sugar to be examined was dissolved in an acid solution made to the desired concentration from C.P. H_2SO_4. Samples were heated in 100-ml. volumes and aliquots withdrawn at intervals and immediately cooled to 0°. Appropriate dilutions were made in volumetric flasks and the absorption curves run at room temperature.

Separation of D-Xylose into Ether-soluble and Ether-insoluble Fractions after Treatment with 8.2 N H_2SO_4.—One gram of D-xylose was dissolved in 100 ml. of 8.2 N H_2SO_4 and the solution heated for 3 hours in the boiling water-bath. The solution was then chilled to 0° (ice and water) and continuously extracted with 100 ml. of ether for 18 hours. The ether solution was then cooled, adjusted to 100 ml. in a volumetric flask, and an aliquot diluted 1:400 with ether. The absorption spectrum was determined on the diluted ether solution (Fig. 3). The absorption spectrum was obtained from the aqueous phase without dilution.

Reaction of L-Arabinose with 20 N H_2SO_4.—Twenty-five grams of L-arabinose which had an optical rotation of $[\alpha]^{21}\mathrm{D}$ $+105°$ (H_2O, *c* 9) after the solution had reached equilibrium[32] was dissolved in 50 ml. of 20 N H_2SO_4. The solution

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(22) D. L. Williams and A. P. Dunlop, *Ind. Eng. Chem.*, **40**, 239 (1948).

(23) R. E. Reeves and J. Munro, *Ind. Eng. Chem., Anal. Ed.*, **12**, 551 (1940).

(24) O. L. Brady and G. V. Elsmie, *Analyst*, **51**, 77 (1926).

(25) Reagent grade obtained from Merck and Co., Inc., Rahway, N. J.

(26) No. 535 obtained from the Johns–Manville Co., New York, N. Y.

(27) A. P. Dunlop and F. N. Peters, "The Furans" (A.C.S. Monograph) Reinhold Publishing Corp., New York, N. Y., 1953, pp. 272 ff.

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(30) The optical rotations were obtained after the solutions had equilibrated for 48 hours at room temperature.

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(32) C. S. Hudson and E. Yanovsky, THIS JOURNAL, **39**, 1013 (1917).

was immediately extracted with approximately 500 ml. of ether in a continuous extractor for 26 hours at room temperature. At the end of this time the ether solution was cooled and shaken with 500 ml. of Brady reagent[24] for 10 minutes. The ether was removed at room temperature under an air jet and the insoluble 2,4-dinitrophenylhydrazones which precipitated were removed by filtration on a fritted glass filter; weight 450 mg.

Chromatography of the 2,4-Dinitrophenylhydrazones.—The crude mixture of 2,4-dinitrophenylhydrazones was dissolved in a 1:2 (by volume) benzene–petroleum ether (b.p. 60–90°) mixture and chromatographed after the manner of Roberts and Green[33] on silicic acid[25]–Celite[26] (3:1 by weight) on a 43 × 250 mm. column. The column was washed with 200 ml. of 1:1 (by volume) benzene–petroleum ether (b.p. 60–90°) and then developed with 75 ml. of benzene containing 0.5 ml. of *t*-butyl alcohol per liter. The column showed the following bands: A, orange-red in color, approximately 3 cm. in width at a distance of approximately 3 cm. from the top of the column; B, orange-yellow in color, approximately 1.5 cm. in width and 8 cm. from the top of the column; C, orange in color, approximately 2 cm. in width and 10.5 cm. from the top of the column; D, orange in color, approximately 3 cm. in width and approximately 13 cm. from the top of the column. The column was extruded and the zones cut and eluted with ethanol.

Identification of Chromatographically Separated 2,4-Dinitrophenylhydrazones.—The contents of each zone was crystallized from ethanol. The empirical formulas and physical constants[34] showed the compounds to be the 2,4-dinitrophenylhydrazones of furfuraldehyde, formaldehyde, crotonaldehyde and acetaldehyde. A mixed melting point confirmed the identity of the compounds.

Identical results were obtained when D-xylose, D-lyxose and D-ribose were treated in the same way.

Acknowledgment.—We wish to thank Mrs. P. P. Wheeler for the microanalyses and Mr. L. S. Hafner for technical assistance, and to thank Dr. C. Schuerch of the State University of New York, College of Forestry, for his helpful criticism of the manuscript.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, NORTHWESTERN UNIVERSITY]

The Stereoisomers of 10-Hydroxymethyl-2-decalol[1]

BY L. S. MINCKLER, A. S. HUSSEY AND ROBERT H. BAKER

RECEIVED AUGUST 15, 1955

The preparation of the four stereoisomers of 10-hydroxymethyl-2-decalol starting from 10-carbethoxy-γ-$\Delta^{1,9}$-2-octalone is described. Configurational assignments for each of these isomers are made.

In an earlier communication having to do with the stereochemistry of angularly substituted methyldecalols,[2] we described a 10-hydroxymethyl-2-decalol which melted at 142°. This was derived from a 10-carboxy-2-decalol which readily formed a lactone; hence the hydroxymethyl and hydroxyl groups were known to be *cis* to one another. The ring fusion of this series of compounds recently has been shown to be *trans*.[3-5] As a consequence, this diol is now correctly designated *cis*-10-hydroxymethyl-2-*trans*-decalol[6] (I). We describe here the synthesis and configurational assignment of the other three isomeric diols: *trans*-10-hydroxymethyl-2-*trans*-decalol (II), *cis*-10-hydroxymethyl-2-*cis*-decalol (III) and *trans*-10-hydroxymethyl-2-*cis*-decalol (IV). All of these have been prepared from the same starting material, 10-carbethoxy-$\Delta^{1,9}$-2-octalone (V).[2,3,7]

The *trans–trans*-diol II was obtained in the following way. 10-Carbethoxy-2-*trans*-decalone (VI),[2,3,7] from V by catalytic reduction, was reduced with sodium borohydride to an hydroxyester. This hydroxyester could be converted to the hydroxyacid and the lactone previously described[2,3,5] by saponification, or to I by reduction with lithium aluminum hydride. It was therefore *cis*-10-carbethoxy-2-*trans*-decalol (VII). *trans*-10-Carbethoxy-2-*trans*-decalol was obtained as its acetate ester VIII when the *p*-toluenesulfonate derivative of VII was treated with potassium acetate in acetic acid. Reduction of VIII with lithium aluminum hydride gave *trans*-10-hydroxymethyl-2-*trans*-decalol (II), m.p. 117.5–119°. A second crystalline modification of II melted at 128–129°, re-melted at 117–118°.

The *cis–cis*-diol III was obtained from V simply by varying the order of the steps which lead to I[2]. Reduction of V to *cis*-10-hydroxymethyl-$\Delta^{1,9}$-2-octalol (IX) by means of lithium aluminum hydride was followed by catalytic reduction to an hydroxymethyldecalol, m.p. 124–125°. This diol was different from I or II, and that it was the *cis–cis* diol III was confirmed in the following way. With sodium borohydride, V was reduced to the hydroxyester X. When X was reduced catalytically to the decalin derivative and the latter, without isolation, treated with lithium aluminum hydride, compound I was formed. When X was treated in the reverse order (that is, with lithium aluminum hydride and then reduced catalytically), the diol which melts at 124–125° was obtained. This diol must therefore have a *cis* relationship of hydroxymethyl and hydroxyl groups and a *cis* ring fusion.

The *trans–cis*-diol IV was obtained from V by still another variation in the order of the steps. The keto group was first blocked by the formation of the dioxolan derivative XI.[5,8] The ester function

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(1) We acknowledge with gratitude a grant from the Research Corporation which made this investigation possible.

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