percentage of oxalic acid that would have been obtained, had no oxidation occurred, was calculated and is indicated in Fig. 2 by the dashed line. The calculated yield of oxalic acid at twenty-four hours is 44.2% of the carbon and at fifty hours, 45.7%. On the same basis the estimated yield of carbon dioxide would remain nearly constant at about 20%. It will also be observed that the yield of water-soluble, ozone-resistant acids became nearly constant with about a 32% conversion of the carbon. Considering the demonstrated resistance of phthalic acid to ozonization under the conditions used and the fact that benzene carboxylic acids have been isolated from other extensive oxidations of bituminous coals, it appears likely that benzene carboxylic acids are present in the ozone-resistant acids. Finally a small but constant amount of acetic acid was formed.

These results would be expected from a polynucleararomatic structure and, experimentally, pyrenequinone was found to yield carbon dioxide, oxalic acid and 1,2,3,4-benzenetetracarboxylic acid. However, the appearance of about 20% of the carbon of the humic acids in the form of carbon dioxide in the first eight hours and apparently none thereafter, except from the oxidation of the oxalic acid present, would not be expected from a polynuclear aromatic structure. Carbon dioxide was obtained from carbon black and the humic acids carbonized to 950°, but only traces in twenty-four hours and no oxalic acid. This resistance to ozonization may be considered to be proof that the humic acids contain no amorphous carbon, but there is also the possibility that the marked insolubility of these carbons was the cause of their unreactivity. Consequently, the humic acids suspended in water in which they are quite insoluble, were ozonized and, although the rate was much slower, the end-products were the same. Also, graphite oxide was ozonized, but was insoluble and unreactive like the carbons. Finally, a sample of the dark brown, water-soluble acids, obtained by oxidizing carbon black with boiling nitric acid, was ozonized. In this case, the brown color was readily destroyed and carbon dioxide, oxalic acid, and ozone-resistant acids were obtained.

Assuming that the brown color of the water-soluble acids was due to unoxidized islands of amorphous carbon, it appears that ozone is capable of attacking such carbon atoms under favorable conditions. Since the structure of amorphous carbon appears to be closely related to the polynuclear aromatic structure,[6] the identification of carbon dioxide, oxalic acid and benzenecarboxylic acids was not surprising. Furthermore, the similarity in behavior of the humic acids and the brown, carbon-black acids toward ozone suggests the possibility that the two acids have similar structures. Whether these are basically aromatic structures or the somewhat more complex structure of amorphous carbon cannot be decided definitely on the basis of the results obtained.

Summary

Both carbonic and oxalic acids appear to be primary products in the ozonization of the humic acids and account for about 65% of the carbon. Practically all of the remaining carbon was converted to almost colorless, water-soluble, ozone-resistant acids. Although carbon black and graphite oxide did not react with ozone appreciably, the brown, water-soluble acids prepared by oxidizing carbon black with nitric acid did react like the humic acids, giving carbonic, oxalic and ozone-resistant acids.

[6] von Steiger, *Ber.*, **53**, 666 (1920).

STATE COLLEGE, PENNSYLVANIA
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1,3-Anhydro-2,4-methylene-D,L-xylitol and Related Compounds

BY RAYMOND M. HANN,[1] NELSON K. RICHTMYER,* HARRY W. DIEHL AND C. S. HUDSON†

An earlier paper[2] from this Laboratory has described the preparation and properties of 2,4:3,5-dimethylene-D,L-xylitol and some of its derivatives, together with its transformation to 2,4-methylenexylitol (a *meso* form) and some of its derivatives. The present communication will describe the results of further research in these two series of compounds.

In the first set of reactions the 2,4-methylenexylitol, upon treatment with benzaldehyde and zinc chloride, yielded a mixed acetal which has been named, in accordance with the system used in the earlier paper, 2,4-methylene-3,5-benzylidene-D,L-xylitol. The free hydroxyl group was readily tosylated, and the tosyloxy group replaced in succession by an iodine and then a hydrogen atom. Subsequent removal of the benzylidene group by acid hydrolysis produced the expected 1-desoxy-2,4-methylene-D,L-xylitol as prisms melting at 52–53°. This value is 103°

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* Harvard University Ph.D. 1927.

† Editorial Board 1938–1944.

[1] Deceased, April 30, 1949.

[2] R. M. Hann, A. T. Ness and C. S. Hudson, THIS JOURNAL, **66**, 670 (1944).

lower than that of the known 1-desoxy-2,4:3,5-dimethylene-D,L-xylitol (155–156°)[2] into which it was transformed smoothly by the action of formaldehyde and hydrochloric acid. A similar difference of 93° was found to exist between the melting points of the 2,4-methylenexylitol (108–109°) and the corresponding 2,4:3,5-dimethylene-D,L-xylitol (201–202°). Thus the introduction of the second methylene acetal ring (3,5) into each of these compounds raises the melting point greatly and in the same magnitude.

In a second set of reactions the 1-tosyl derivative of 2,4:3,5-dimethylene-D,L-xylitol[2] was heated with sodium thiocyanate in acetonylacetone at 120°[3] and thus converted to 1-thiocyano-1-desoxy-2,4:3,5-dimethylene-D,L-xylitol. Treatment of the latter substance with sodium methoxide yielded the corresponding bis-(2,4:3,5-dimethylene-D,L-xylityl) disulfide, while reductive desulfurization with Raney nickel yielded the known 1-desoxy-2,4:3,5-dimethylene-D,L-xylitol.[2] This method of going from a tosylated primary carbinol to a methyl group in the sugar series offers an alternate route to the usual one by way of the iodo derivative followed by catalytic hydrogenation, and may appear to be a more satisfactory approach in those cases where unstable or non-crystalline products are encountered.

The third and most interesting set of reactions also started with 1-tosyl-2,4:3,5-dimethylene-D,L-xylitol (I). The acetolysis of this compound by a mixture of acetic anhydride and glacial acetic acid containing 2% of concentrated sulfuric acid led to a practically quantitative yield of 1-tosyl-2,4-methylene-3-acetoxymethyl-5-acetyl-D,L-xylitol (II); the allocation of the acetoxymethyl group to the secondary hydroxyl and the acetyl group to the primary hydroxyl was based upon studies of the crystalline acetolysis products of the methylene acetals of other polyhydric alcohols, especially 1,3:2,5:4,6-trimethylene-D-mannitol[4] and 2,4:3,5-dimethylene-L-xylitol.[5] Saponification of compound II with aqueous alkali at room temperature consumed two equivalents of reagent, liberating both acetyl and acetoxymethyl groups[4] to form 1-tosyl-2,4-methylene-D,L-xylitol (III). The action of hot alkali removed the tosyl group also and the resulting product melting at 104–105° had the composition of an anhydromethylenexylitol.

Of the three possible formulas for our anhydro compound the ethylenic structure IV was eliminated first because the substance failed to add hydrogen in the presence of a platinum catalyst. Next we attempted to synthesize a compound with structure V through the action of formaldehyde and hydrochloric acid on the known 1,5-anhydroxylitol,[6] but in spite of repeated attempts, even at 100° under pressure, the starting material was recovered unchanged.

Finally we decided to try to make a tosyl derivative and study its behavior toward sodium iodide. Although tosylation at room temperature led to the expected monotosyl derivative, two products were obtained when the reaction was carried out at 70°. The second substance, upon analysis, was found to contain two tosyl groups and a chlorine atom, and apparently had been formed from the monotosyl derivative by reaction with a second molecule of *p*-toluenesulfonyl chloride. This discovery gave us the first clue to the structure of our compound as 1,3-anhydro-2,4-methylene-D,L-xylitol (VI). Although there seems to be no previous example of a 1,3-anhydro ring among the derivatives of the sugar alcohols, the rare 1,3-anhydro or propylene oxide rings which are known among other organic compounds appear to be much less stable than the 1,5-anhydro rings such as occur in polygalitol, styracitol and other anhydrides of sugar alcohols. Consequently the opening of a 1,3-anhydro ring during tosylation would not be unexpected whereas the opening of a 1,5-anhydro ring would probably be unique.

Continuing with the monotosyl derivative, we heated it with sodium iodide in acetonylacetone at 100° for eighteen hours and succeeded in obtaining a crystalline iodine compound in good yield; this would indicate, by the Oldham–Rutherford rule,[7] that the tosyloxy group was attached to the primary carbon atom 5, as in formula VII. However, there has been reported one striking exception to this rule: the tosyloxy groups in 1,4:3,6-dianhydro-2,5-ditosyl-D-mannitol are replaced by iodine atoms upon heating the compound with sodium iodide in acetone at 110° for only three and one-half hours.[8] Consequently we sought and obtained an absolute proof by catalytic reduction of the iodo derivative (VIII) with Raney nickel to the corresponding desoxy compound (IX). Analysis of the latter substance, prisms melting at 64–65°, showed that it contained a C-methyl group, a circumstance which would be possible only if the tosyloxy group had been attached to the primary carbon atom 5; if the anhydro compound had had a 1,5-ring as in formula V, then the corresponding desoxy compound would have had a methylene group at carbon atom 3, and no C-methyl group. Hence the final desoxy compound must be 1,3-anhydro-2,4-methylene-5-desoxy-D,L-xylitol (IX), and the parent anhydro compound was 1,3-anhydro-2,4-methylene-D,L-xylitol (VI).

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[3] See J. F. Carson and W. D. Maclay, This Journal, **70**, 2220 (1948), and A. Müller and A. Wilhelms, *Ber.*, **74**, 698 (1941), for some pertinent references to the thiocyanation of the primary alcohol group in carbohydrates.

[4] A. T. Ness, R. M. Hann and C. S. Hudson, This Journal, **65**, 2215 (1943).

[5] A. T. Ness, R. M. Hann and C. S. Hudson, *ibid.*, **66**, 665 (1944).

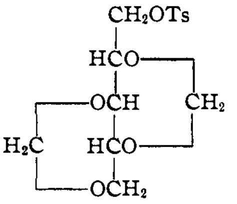
[6] H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **69**, 921 (1947).

[7] J. W. H. Oldham and J. K. Rutherford, *ibid.*, **54**, 366 (1932).

[8] P. Brigl and H. Grüner, *Ber.*, **67**, 1582 (1934); R. C. Hockett, H. G. Fletcher, Jr., E. L. Sheffield, R. M. Goepp, Jr., and S. Soltzberg, This Journal, **68**, 930 (1946).

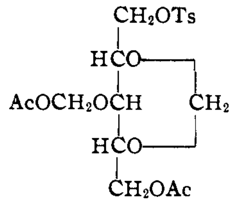
Experimental Part

Substances Prepared from 2,4-Methylenexylitol



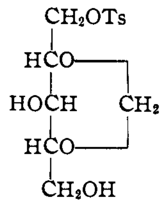
I

1-Tosyl-2,4:3,5-dimethylene-D,L-xylitol[9]



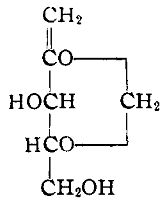
II

1-Tosyl-2,4-methylene-3-acetoxymethyl-5-acetyl-D,L-xylitol



III

1-Tosyl-2,4-methylene-D,L-xylitol



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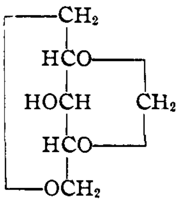
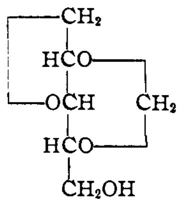
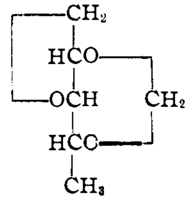


V



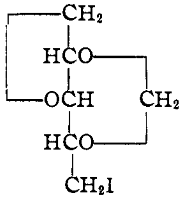
VI

1,3-Anhydro-2,4-methylene-D,L-xylitol



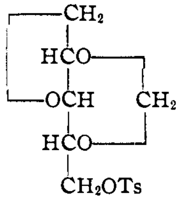
IX

1,3-Anhydro-2,4-methylene-5-desoxy-D,L-xylitol



VIII

1,3-Anhydro-2,4-methylene-5-iodo-5-desoxy-D,L-xylitol



VII

1,3-Anhydro-2,4-methylene-5-tosyl-D,L-xylitol

2,4-Methylene-3,5-benzylidene-D,L-xylitol.—A suspension of 15 g. of powdered 2,4-methylenexylitol,[2] 15 g. of powdered fused zinc chloride and 75 ml. of benzaldehyde was shaken vigorously for five minutes. Most of the solid dissolved as the mixture warmed slightly, then set to a partly crystalline gel. This was diluted with 175 ml. of absolute ethanol and left in the refrigerator for several hours to complete crystallization. The product was filtered, washed with 20 ml. of cold, absolute ethanol followed by 50 ml. of water, and dried in the air to yield 19.1 g. (83%) melting at 185–186°. Upon recrystallization as fine needles from 70 parts of ethanol, the benzylidene derivative melted at 187–188°, a value which was unchanged by two additional recrystallizations. It is readily soluble in cold acetone, moderately soluble in warm benzene, chloroform, dioxane, ethyl acetate, methanol and ethanol, and practically insoluble in ether, petroleum ether and water.

Anal. Calcd. for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 62.07; H, 6.39.

1-Acetyl-2,4-methylene-3,5-benzylidene-D,L-xylitol was prepared from 1 g. of the preceding compound by allowing it to stand overnight in a mixture of 5 ml. each of acetic anhydride and pyridine. The product crystallized readily when the solution was poured over crushed ice; filtered, washed well with water and dried, it weighed 1.1 g. and melted at 155–156°. For analysis it was recrystallized several times from 40 parts of hot absolute ethanol as fine needles, the melting point remaining unchanged.

Anal. Calcd. for $C_{15}H_{18}O_6$: C, 61.22; H, 6.16. Found: C, 61.32; H, 6.17.

1-Benzoyl-2,4-methylene-3,5-benzylidene-D,L-xylitol was prepared by adding 1 g. of benzoyl chloride to a solution of 1 g. of 2,4-methylene-3,5-benzylidene-D,L-xylitol in 10 ml. of pyridine. After standing overnight the mixture was poured on ice and 1.5 g. of crystalline material obtained, m. p. 169–170°. After two recrystallizations from 130 parts of absolute ethanol the cottony needles melted at 173–174°.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.66; H, 5.89.

1-Tosyl-2,4-methylene-3,5-benzylidene-D,L-xylitol was obtained in nearly quantitative yield by the addition of 5.6 g. (1.5 molecular equivalents) of *p*-toluenesulfonyl chloride to an ice-cold solution of 5 g. of 2,4-methylene-3,5-benzylidene-D,L-xylitol in 50 ml. of pyridine. The next morning the mixture was poured into ice-water, the product separating at once in crystalline form; filtered, washed and dried, it weighed 7.9 g. and melted at 146–147°. One recrystallization from 40 parts of ethanol raised the melting point of the prismatic needles to 149–150°, where it remained unchanged after two additional recrystallizations.

Anal. Calcd. for $C_{20}H_{22}O_7S$: C, 59.10; H, 5.46. Found: C, 58.99; H, 5.71.

1-Iodo-1-desoxy-2,4-methylene-3,5-benzylidene-D,L-xylitol.—Replacement of the tosyloxy group in the preceding compound by an iodine atom was effected by heating 5 g. of the tosyl compound with 5 g. of sodium iodide in 50 ml. of acetonylacetone containing 0.1 g. of sodium bicarbonate to prevent possible cleavage of the benzylidene residue. A temperature of 120° for forty-eight to seventy-two hours, followed by filtration of the separated sodium *p*-toluenesulfonate from the cooled solution and dilution of the filtrate with water, yielded 4.3 g. (theory, 4.5 g.) of product. The iodo compound was purified by recrystallization from 30 parts of ethanol; the small needles melted at 165–166°.

Anal. Calcd. for $C_{13}H_{15}IO_4$: C, 43.11; H, 4.17. Found: C, 43.23; H, 4.46.

1-Desoxy-2,4-methylene-3,5-benzylidene-D,L-xylitol.—Each 3-g. batch of iodo compound in 200 ml. of methanol containing 9 ml. of *N* sodium hydroxide and 4 g. of Raney nickel was shaken at about 25° with hydrogen under a slight positive pressure. The theoretical amount of hydrogen required to replace the iodine atom was absorbed within thirty minutes. The catalyst was removed by filtration, and the desoxy compound crystallized by concentration of the methanol solution. The yield of product melting at 139–140° was nearly quantitative, a total of 17.6 g. being obtained from 28 g. of the iodo compound. For analysis the substance was recrystallized twice from 10 parts of absolute ethanol as small needles melting at 140–141°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.31; H, 7.04.

1-Desoxy-2,4-methylene-D,L-xylitol.—Mild acid hydrolysis of 12.2 g. of the preceding benzylidene compound was complete after heating with 150 ml. of 0.01 *N* sulfuric

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(9) To save space in writing the formulas of racemic substances only the D-form has been shown.

acid for three hours on the steam-bath. The liberated benzaldehyde was removed by concentration *in vacuo*, more water being added as necessary, and the sulfuric acid was neutralized with aqueous barium hydroxide solution. The clear filtrate was then concentrated *in vacuo* to a dry sirup which crystallized when stirred with ether. The product, separated by filtration in the cold room (−5°), weighed 7.0 g. (92%) and melted at 49–51°. It was recrystallized from 250 ml. of ether to yield 5.3 g. (first crop) of chunky prisms melting at 52–53°. The substance is preferably preserved in a desiccator, for in warm humid weather it tends to be hygroscopic.

Anal. Calcd. for $C_6H_{12}O_4$: C, 48.64; H, 8.17; CH_3 (to C), 10.14. Found: C, 48.64; H, 8.19; CH_3 (to C), 10.07.

1-Desoxy-2,4-methylene-3,5-ditosyl-D,L-xylitol.—The introduction of two tosyl groups into 1-desoxy-2,4-methylene-D,L-xylitol was effected by dissolving 1 g. of the compound in 5 ml. of pyridine and adding 4 g. (3.1 molecular equivalents) of *p*-toluenesulfonyl chloride. After standing overnight at room temperature, the mixture was poured on crushed ice; crystallization occurred at once. The product, washed with water and dried, was recrystallized from 7 parts of ethanol to yield 2.7 g. (88%) of small, elongated prisms melting at 112–113°. The melting point was unchanged by two additional recrystallizations from 10 parts of ethanol.

Anal. Calcd. for $C_{20}H_{24}O_8S_2$: C, 52.62; H, 5.30. Found: C, 52.65; H, 5.40.

1-Desoxy-2,4-methylene-5-tosyl-D,L-xylitol.—To a stirred solution of 2 g. of 1-desoxy-2,4-methylene-D,L-xylitol in 25 ml. of pyridine, cooled in ice and salt, was added dropwise over a period of thirty-five minutes a solution of 3.1 g. (1.2 molecular equivalents) of *p*-toluenesulfonyl chloride. After standing another half-hour in the bath and two hours at room temperature the mixture was poured on ice. Crystals appeared within fifteen minutes; these were filtered (1.85 g.) and an additional amount (0.31 g.) obtained by extraction of the aqueous solution with chloroform in the usual manner. By fractional crystallization from ethanol the product was separated to yield 0.3 g. of the ditosyl derivative described above and 1.2 g. (30%) of the new monotosyl derivative. The latter crystallized from 7 parts of ethanol in small plates which when pure melted at 145–146°. The tosyl group was assigned to the 5- rather than to the 2-position only by analogy with other unimolecular tosylations.

Anal. Calcd. for $C_{13}H_{18}O_6S$: C, 51.64; H, 6.00. Found: C, 51.69; H, 6.13.

Transformation of 1-Desoxy-2,4-methylene-D,L-xylitol to 1-Desoxy-2,4,:3,5-dimethylene-D,L-xylitol.—A mixture of 1 g. of the monomethylene compound, 2 ml. of 37% formaldehyde and 2 ml. of concentrated hydrochloric acid was heated for two hours at 50°, then cooled and diluted with 20 ml. of ethanol. The crystals which appeared were permitted to grow in amount for three hours in the refrigerator before being filtered. The 0.56 g. thus obtained was increased to 0.82 g. (76%) by a second crop obtained by concentration of the mother liquor. After one recrystallization from 10 parts of ethanol the product was identified by melting point and mixed melting point of 156–157° as the 1-desoxy-2,4:3,5-dimethylene-D,L-xylitol described by Hann, Ness and Hudson.[2]

Substances Prepared from 2,4:3,5-Dimethylene-D,L-xylitol

1-(α-Naphthylcarbamyl)-2,4:3,5-dimethylene-D,L-xylitol.—To 0.9 g. of 2,4:3,5-dimethylene-D,L-xylitol[2] in 20 ml. of pyridine was added 1 ml. of α-naphthyl isocyanate and the mixture boiled for two hours under a reflux condenser. The solution was cooled, filtered from 0.2 g. of di-α-naphthylurea and the filtrate evaporated to dryness in a current of air. The residue, upon crystallization from 250 ml. of absolute ethanol, yielded 0.4 g. of fine needles melting at 211–212°, a value which was not changed by recrystallization from 120 ml. of the same solvent. The compound is soluble in hot chloroform, dioxane, ethyl acetate and toluene, sparingly soluble in cold acetone, hot methanol and ethanol, and practically insoluble in cold benzene, chloroform, dioxane, ether, ethyl acetate, methanol, ethanol, toluene and water.

Anal. Calcd. for $C_{18}H_{19}NO_6$: C, 62.60; H, 5.55; N, 4.06. Found: C, 62.57; H, 5.76; N, 4.01.

1-Thiocyano-1-desoxy-2,4:3,5-dimethylene-D,L-xylitol.—A mixture of 16 g. of 1-tosyl-2,4:3,5-dimethylene-D,L-xylitol,[2] 16 g. of dried sodium thiocyanate (4.1 molecular equivalents) and 160 ml. of acetonylacetone was heated in an oven for forty-six hours at 120°. After cooling to room temperature, 8.6 g. (theory, 9.4 g.) of sodium *p*-toluenesulfonate was removed by filtration and the filtrate concentrated to a small volume by a current of air, at first on the steam-bath and finally at room temperature. The addition of 50 ml. of cold water resulted in the crystallization of 6.2 g. of product, with a second crop being obtained by similar concentration of the mother liquor to bring the total yield to 9.2 g. (87%). The compound was pure after one recrystallization from hot water. For analysis a portion was thrice recrystallized from 15 parts of ethanol, separating as shining, plate-like prisms melting at 147–148°. It is readily soluble in cold acetone, less soluble in methanol.

Anal. Calcd. for $C_8H_{11}NO_4S$: C, 44.23; H, 5.10; S, 14.76. Found: C, 44.38; H, 5.24; S, 14.93.

Bis-(2,4:3,5-dimethylene-D,L-xylityl) Disulfide.—The thiocyano compound was converted readily to the corresponding disulfide by dissolving 0.5 g. of it in 31.8 ml. of 0.145 *N* sodium methoxide (2 molecular equivalents) and filtering off the silky needles which began to separate within a few hours. The yield was 0.28 g. (64%) of disulfide which, after two recrystallizations from methanol, melted at 192–193°. The compound is readily soluble in chloroform, fairly soluble in acetone and benzene, and less soluble in methanol and ethanol.

Anal. Calcd. for $C_{14}H_{22}O_8S_2$: C, 43.96; H, 5.80; S, 16.77. Found: C, 44.07; H, 5.80; S, 16.52.

Reductive Desulfurization of 1-Thiocyano-1-desoxy-2,4:3,5-dimethylene-D,L-xylitol.—A solution of 5 g. of the thiocyano compound in 350 ml. of 70% ethanol was heated on the steam-bath with about 120 g. of Raney nickel for two hours. The Raney nickel was removed by filtration and washed thoroughly by extracting with three 300-ml. portions of water, boiling for thirty minutes each time. The combined aqueous alcohol solutions were concentrated *in vacuo* to yield 2.6 g. (70%) of 1-desoxy-2,4:3,5-dimethylene-D,L-xylitol melting at 156–157°; the product showed no depression in melting point when mixed with an authentic sample.[2]

1-Mesyl-2,4:3,5-dimethylene-D,L-xylitol.—A solution of 5 g. of 2,4:3,5-dimethylene-D,L-xylitol in 100 ml. of pyridine was cooled in an ice-bath and to it was added 3.3 ml. of methanesulfonyl chloride. After standing overnight, the reaction mixture was shaken for six hours, and then filtered to remove 1.7 g. of water-soluble material melting at 182–184°. The filtrate was concentrated in a current of air to a heavy sirup which began to crystallize spontaneously. A small amount of water was added and 4.5 g. of product separated; extraction of the mother liquor with chloroform yielded an additional 1.3 g. One recrystallization from 6 parts of ethanol furnished 5.0 g. (69%) of elongated prisms melting at 102–103°, and two additional recrystallizations raised the melting point to 103–104°. The mesyl derivative is soluble in acetone, chloroform, hot dioxane, hot ethanol and hot ethyl acetate, less soluble in methanol and water, and practically insoluble in hot benzene and ether.

Anal. Calcd. for $C_8H_{14}O_7S$: C, 37.79; H, 5.55; S, 12.61. Found: C, 38.04; H, 5.80; S, 12.59.

1-Mesyl-2,4-methylene-3-acetoxymethyl-5-acetyl-D,L-xylitol.—One gram of the preceding mesyl derivative was ground to a fine powder and shaken in an ice-bath for fifteen minutes with 5 ml. of an ice-cold solution prepared by adding 1 ml. of concentrated sulfuric acid to 35 ml. of acetic anhydride and 15 ml. of acetic acid. Crystallization occurred readily when the solution was poured on cracked ice; the product, including a small amount obtained by extraction of the mother liquor with chloroform, was recrystallized twice from 20 parts of absolute ethanol as long needles weighing 1.0 g. (71%) and melting at 112–113°. The allocation of the acetoxymethyl and acetyl groups to carbon atoms 3 and 5, respectively, follows from experiences with similar acetolyses.[4,5]

Anal. Calcd. for $C_{12}H_{20}O_{10}S$: C, 40.44; H, 5.66; S, 9.00. Found: C, 40.29; H, 5.55; S, 8.82.

1-Tosyl-2,4-methylene-3-acetoxymethyl-5-acetyl-D,L-xylitol (II).—Fourteen grams of powdered 1-tosyl-2,4:3,5-dimethylene-D,L-xylitol (I)[2] was shaken for fifteen minutes in an ice-bath with 75 ml. of an ice-cold solution prepared by adding 2 ml. of concentrated sulfuric acid to a cold mixture of 70 ml. of acetic anhydride and 30 ml. of glacial acetic acid. The reaction mixture was poured over 500 g. of finely cracked ice and stirred for thirty minutes to promote crystallization. The product, filtered, washed with water and dried, weighed 17.5 g. (95%). One recrystallization from 5 parts of ethanol yielded 16.6 g. of prismatic needles whose melting point of 79–80° was not changed by two additional recrystallizations of a small sample for analysis.

Anal. Calcd. for $C_{18}H_{24}O_{10}S$: C, 49.99; H, 5.59; S, 7.41. Found: C, 50.05; H, 5.75; S, 7.56.

1-Tosyl-2,4-methylene-D,L-xylitol (III).—To a solution of 4.3 g. of 1-tosyl-2,4-methylene-3-acetoxymethyl-5-acetyl-D,L-xylitol (II) in 100 ml. of acetone was added 30 ml. of *N* aqueous sodium hydroxide. After standing at 20° for five hours the solution was neutralized to phenolphthalein with 91 ml. of 0.1 *N* sulfuric acid; the consumption of 20.9 ml. of *N* alkali (2.09 molecular equivalents) thus corresponded to the loss of the acetyl and the acetoxymethyl groups. The solution was evaporated in a current of air to about 50 ml. and the crystals (1.8 g.) removed by filtration. Further concentration of the mother liquor increased the yield to 2.9 g. (92%) of product melting at 128–129°. For analysis the 1-tosyl-2,4-methylene-D,L-xylitol was recrystallized twice from 12 parts of ethanol as fine needles melting at 129–130°.

Anal. Calcd. for $C_{13}H_{18}O_7S$: C, 49.05; H, 5.70. Found: C, 49.11; H, 5.90.

1,3-Anhydro-2,4-methylene-D,L-xylitol (VI).—Although the anhydro compound may be prepared directly by the action of hot alkali on 1-tosyl-2,4-methylene-3-acetoxymethyl-5-acetyl-D,L-xylitol (II), better yields are obtained by carrying out the reaction in two steps, the first of which has just been described. In the second step, 11.1 g. of the 1-tosyl-2,4-methylene-D,L-xylitol (III) was heated in a mixture of 100 ml. of acetone, 100 ml. of water and 42 ml. of *N* sodium hydroxide for one hour on the steam-bath under a reflux condenser. The solution was cooled, then neutralized with 7.1 ml. of *N* sulfuric acid. The consumption of 34.9 ml. of *N* alkali corresponded exactly to that required for the elimination of one equivalent of *p*-toluenesulfonic acid. The solution was concentrated to dryness with a current of air and the anhydro compound isolated by extraction of the sodium salts with three 25-ml. portions of acetone. Concentration of the acetone solution to a small volume and the addition of ether yielded, in four fractions, a total of 4.7 g. (92%) of material melting between 100 and 104°. Two recrystallizations from 3 parts of absolute ethanol furnished analytically pure compound as elongated plates melting at 104–105°.

The attempted hydrogenation of 1 g. of compound in 100 ml. of methanol with 0.1 g. of Adams platinum oxide catalyst was unsuccessful.

Anal. Calcd. for $C_6H_{10}O_4$: C, 49.31; H, 6.90. Found: C, 49.32; H, 6.86.

1,3-Anhydro-2,4-methylene-5-tosyl-D,L-xylitol (VII).—Tosylation of 12 g. of the preceding compound by the action of 40 g. of *p*-toluenesulfonyl chloride (2.5 molecular equivalents) in 180 ml. of pyridine overnight at 25°, then poured on ice, yielded a crystalline product readily. It was purified by recrystallization from 5 parts of ethanol; the clear prisms weighed 20.5 g. (83%) and melted at 82–83°.

Anal. Calcd. for $C_{13}H_{16}O_6S$: C, 51.99; H, 5.37. Found: C, 52.04; H, 5.45.

Chloroditosyl-2,4-methylenexylitol.—In a preliminary tosylation experiment 2.1 g. of the compound now known as 1,3-anhydro-2,4-methylene-D,L-xylitol was allowed to stand for three days at room temperature in 30 ml. of pyridine containing 6.6 g. of *p*-toluenesulfonyl chloride, and then heated for eight hours at 70°. The crude product obtained by pouring the reaction mixture on ice weighed 4.7 g. and melted at 73–80°. Careful fractionation from ethanol showed it to be a mixture from which was obtained 2.6 g. of the prismatic monotosyl derivative melting at 82–83° and 1.1 g. of a less soluble compound which crystallized in needles. The latter compound was purified by recrystallization from 16 parts of ethanol, melted at 124–125°, gave a strong test for halogen, and had the composition of a chloroditosylmethylenexylitol. No attempt was made to locate the chlorine atom or the second tosyl group in this compound.

Anal. Calcd. for $C_{20}H_{23}ClO_8S_2$: C, 48.92; H, 4.72; S, 13.06. Found: C, 48.74; H, 4.61; S, 13.58.

1,3-Anhydro-2,4-methylene-5-iodo-5-desoxy-D,L-xylitol (VIII).—Sixteen grams of 1,3-anhydro-2,4-methylene-5-tosyl-D,L-xylitol (VII) was heated with 16 g. of sodium iodide in 160 ml. of acetonylacetone in an oven at 100° for eighteen hours. The 6.9 g. of precipitated sodium *p*-toluenesulfonate being considerably less than the 10.3 g. expected by theory, the reaction mixture was heated for an additional twenty-eight hours and the yield of sodium *p*-toluenesulfonate increased to 10.0 g. The desired iodo compound was isolated by a combination of concentration *in vacuo* and precipitation by water for a total yield of 12 g. (88%) melting at 97–98°. Upon recrystallization from 4 parts of ethanol it separated in long prismatic needles melting at 99–100°.

Anal. Calcd. for $C_6H_9IO_3$: C, 28.14; H, 3.54. Found: C, 28.18; H, 3.77.

1,3-Anhydro-2,4-methylene-5-desoxy-D,L-xylitol (IX).—Hydrogenation of 2.3 g. of the iodo compound was carried out in 200 ml. of methanol in the presence of 4 g. of Raney nickel and 9 ml. of *N* sodium hydroxide. The reaction was completed with the absorption of one molecular equivalent of hydrogen within thirty minutes. The neutral solution was filtered from the catalyst and concentrated to dryness *in vacuo*. The product was extracted from the residual sodium iodide with ether which upon concentration yielded 0.43 g. (37%) of elongated prisms melting at 64–65°; whether the low yield was due to absorption on the catalyst or to volatility of the compound was not determined. It was recrystallized from 10 parts of ether without change in melting point.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.75; CH_3 (to C), 11.55. Found: C, 55.47; H, 7.85; CH_3 (to C), 11.40.

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Summary

2,4-Methylenexylitol has been converted through the mixed acetal 2,4-methylene-3,5-benzylidene-D,L-xylitol, by a series of reactions, to 1-desoxy-2,4-methylene-D,L-xylitol.

Reductive desulfurization with Raney nickel of 1-thiocyano-1-desoxy-2,4:3,5-dimethylene-D,-L-xylitol to 1-desoxy-2,4:3,5-dimethylene-D,L-xylitol has established a new method for the prepara-

tion of desoxy compounds from primary hydroxyl groups.

The action of alkali on 1-tosyl-2,4-methylene-D,L-xylitol has resulted in the formation of a new 1,3-anhydro ring type among the sugar alcohol derivatives. The structure of the product as 1,3-anhydro-2,4-methylene-D,L-xylitol has been established conclusively.

A total of twenty-one new derivatives of 2,4-methylenexylitol and 2,4:3,5-dimethylene-D,L-xylitol have been described.

BETHESDA, MARYLAND RECEIVED OCTOBER 21, 1949

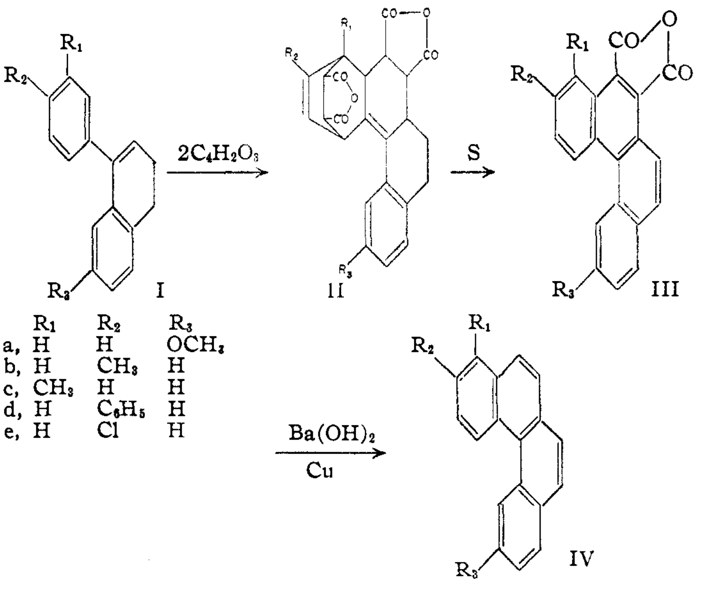
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Condensation of Phenylcycloalkenes with Maleic Anhydride. II. Synthesis of Substituted 3,4-Benzphenanthrenes[1]

BY JACOB SZMUSZKOVICZ[2] AND EDWARD J. MODEST[3]

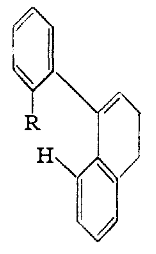
In continuation of our work on the reaction of phenylcycloalkenes with maleic anhydride,[4] we have successfully condensed various substituted dihydronaphthalenes with maleic anhydride and isolated the bis-adducts, which were dehydrogenated and then decarboxylated.

In case Ic the fact that the initial molecule of maleic anhydride adds to a position ortho rather than para to the methyl group was proved by decarboxylation of IIIc to the known 8-methyl-3,4-benzphenanthrene.[5]



	R_1	R_2	R_3
a,	H	H	OCH_3
b,	H	CH_3	H
c,	CH_3	H	H
d,	H	C_6H_5	H
e,	H	Cl	H

Maleic anhydride fails to add to 1-(*o*-tolyl)-3,4-dihydronaphthalene (Va) and to 1-(*o*-anisyl)-3,4-dihydronaphthalene (Vb), even under forcing conditions (220°).



V a, R = CH_3
b, R = OCH_3

A possible explanation for this lack of reactivity is that steric hindrance between the ortho substituent on the phenyl ring and the hydrogen atom at the peri position of the dihydronaphthalene ring forces the diene system out of coplanarity. Newman and Wheatley[6] have shown that optical activity of the 4,5-phenanthrene type is a result of a similar kind of steric interaction.

On decarboxylation of IIIa, IIId and IIIe, we obtained the new compounds 6-methoxy-, 7-phenyl- and 7-chloro-3,4-benzphenanthrene, respectively.

When there is a para methoxy substituent in the phenyl ring, the bis-adduct formed (VI) contains an enol–ether system which is easily ketonized by hot mineral acid.

A comparison of the properties of the two ketonized products reveals distinct dissimilarities. VIIb forms a semicarbazone but VIIa does not. Furthermore the ultraviolet absorption spectrum[7] of VIIb has maxima at 254 mμ (log E 4.04) and 293 mμ (log E 3.60), whereas that of VIIa exhibits only one maximum, at 253 mμ (log E 4.12). The maxima at 253 and 254 mμ are undoubtedly due to absorption of the styrene type.[8,9] The maximum at 293 mμ is due to keto-group absorption, the high value of the extinction coefficient arising from the superimposition effect.

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[4] Szmuszkovicz and Modest, THIS JOURNAL, **70**, 2542 (1948).

[5] Hewett, *J. Chem. Soc.*, 1286 (1938).

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[7] The ultraviolet absorption spectra of aqueous solutions of VIIa and VIIb were measured with a Beckman model DU quartz spectrophotometer.

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