80% acetic acid and then treating the hot solution with boiling glacial acetic acid. The *p*-sulfophenylarsonic acid crystallized in the form of colorless, glistening needles; yield 2.5 g. When heated, the product gradually darkens but remains solid up to 300°. It is insoluble in ether, acetone and benzene; soluble in alcohol.

Anal. Calcd. for $C_6H_7O_6AsS$: As, 26.56. Found: As, 26.51.

Sodium *p*-Sulfophenyldiiodoarsine.—Ten cc. of 50% hydriodic acid was added to a hot solution of 2 g. of sodium *p*-sulfophenylarsonic acid in 5 cc. of water. The crystalline iodoarsine began precipitating immediately. The mixture was filtered after cooling thoroughly and the product washed first with glacial acetic acid and then with acetone. The yield was 2 g. after recrystallizing from 80% acetic acid. It is insoluble in cold glacial acetic acid and alcohol but readily soluble in water. When heated the compound liberates vapors of iodine.

Anal. Calcd. for $C_6H_4O_3AsI_2SNa$: As, 14.75; I, 49.98. Found: As, 14.65; I, 49.76.

Sodium *p*-Sulfophenyldibromoarsine.—A solution prepared from 10 g. of sodium *p*-sulfophenylarsonic acid, 30 cc. of water, 20 cc. of 48% hydrobromic acid and a trace of hydriodic acid was saturated with sulfur dioxide at room temperature. The mixture was then concentrated on the steam-bath to about 20 cc., chilled in ice and the product removed by filtration; 8.5 g. of sodium *p*-sulfophenyldibromoarsine was obtained after recrystallizing from glacial acetic acid–ethyl acetate mixture. The product is readily soluble in alcohol and water.

Anal. Calcd. for $C_6H_4O_3AsBr_2SNa$: As, 18.10; Br, 38.62. Found: As, 18.07; Br, 38.36.

The Piperidine Salt of *p*-Sulfophenylarsylene N-Pentamethylenedithiocarbamate.—To a hot soluiton of 0.5 g. of sodium *p*-sulfophenyldiiodoarsine in 13 cc. of 50% alcohol there was added a hot solution of 0.5 g. of the piperidine salt of N-pentamethylenedithiocarbamic acid in 25 cc. of alcohol. The colorless needles which formed were removed by filtration and washed repeatedly with cold 95% alcohol. The product weighed 0.3 g. and when heated decomposed at 230–232°. The compound is insoluble in ether, acetone and benzene.

Anal. Calcd. for $C_{23}H_{36}O_3N_3AsS_5$: As, 11.75. Found: As, 12.01.

Sodium *p*-Sulfophenylarsine Oxide.—Five grams of sodium hydroxide was added to as olution of 15 g. of sodium *p*-sulfophenyldibromoarsine in 100 cc. of water and the solution boiled under a reflux condenser for fifteen minutes. The solution was then cooled, made acid to congo red paper with 37% hydrochloric acid and allowed to evaporate at room temperature. After several days a heavy mass of large colorless crystals was obtained which weighed 8 g. The product, containing three molecules of water, was purified by dissolving in water, concentrating the solution in a desiccator over sulfuric acid to a small volume and recovering the crystalline residue.

Anal. Calcd. for $C_6H_4O_4AsSNa{\cdot}3H_2O$: As, 23.11. Found: As, 23.00.

The product effloresced at room temperature and was completely dehydrated by heating to 200° for four hours in an oil-bath under reduced pressure.

Anal. Calcd. for $C_6H_4O_4AsSNa$: As, 27.74. Found: As, 27.81.

On adding 10 cc. of 0.25 *N* silver nitrate solution to a hot solution of 0.52 g. of sodium *p*-sulfophenylarsine oxide in 10 cc. of water, a silver salt of *p*-sulfophenylarsine oxide crystallized on slight cooling; yield 0.5 g.

Summary

The preparation of sodium *p*-sulfophenylarsonic acid by the Bart reaction and a method for the purification of the free acid have been described. The following derivatives and salts have been prepared: barium *p*-sulfophenylarsonic acid, the piperidine salt of *p*-sulfophenylarsylene N-pentamethylenedithiocarbamate, sodium *p*-sulfophenyldiiodo and -dibromoarsine and sodium *p*-sulfophenylarsine oxide.

SAN FRANCISCO, CALIF. RECEIVED JUNE 20, 1938

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Cleavage of the Carbon Chain of α-Methyl-*d*-lyxopyranoside by Oxidation with Periodic Acid[1]

BY W. DAYTON MACLAY AND C. S. HUDSON

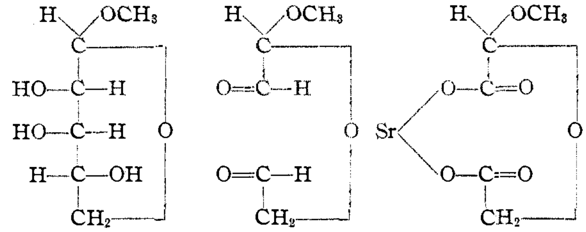
The known α-methyl-*d*-lyxoside (m. p. 108–109°, $[\alpha]^{20}_D + 59.4°$ in water)[2] has been shown by Hirst and Smith[3] through methylation methods to be a pyranoside and it is regarded as the alpha form because it is more dextrorotatory than *d*-lyxose ($[\alpha]^{20}_D -14°$, final); under this classification its structure is (I). It is to be expected that the oxidation of this substance by periodic acid will proceed in the manner that has been demonstrated in the case of the alpha forms of the methyl pyranosides of *d*-xylose and *d*-arabinose[4] to produce the dialdehyde (II); the latter substance, on oxidation by bromine water in the presence of strontium carbonate, should be oxi-

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) Phelps and Hudson, THIS JOURNAL, **48**, 505 (1926).

(3) Hirst and Smith, *J. Chem. Soc.*, 3147 (1928).

(4) Jackson and Hudson, THIS JOURNAL, **59**, 994 (1937).



(I) α-Methyl-*d*-lyxopyranoside (II) D′-Methoxy-diglycolic aldehyde (III) Strontium D′-methoxy-diglycolate

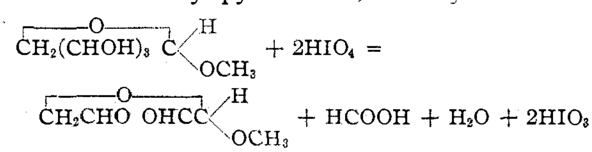
dized to the strontium salt (III), which has been obtained from the xylose and arabinose pyranosides. The experiments have borne out these expectations fully and the crystalline strontium salt, which has been obtained in a yield of 76%, proves to be identical with that which results from the xylose and arabinose α-methyl pyranosides. The result therefore confirms the conclusion from methylation data that the lyxoside is a pyranoside and also proves that it is of the alpha classification, as was previously inferred from the comparison of its rotation with that of lyxose.[5]

TABLE I

COMPARISON OF OXIDATION PRODUCTS OF α-METHYL-*d*-LYXOSIDE WITH THOSE OF α-METHYL-*d*-ARABINOSIDE AND α-METHYL-*d*-XYLOSIDE

Substance	Methyl glycoside $[\alpha]^{20}_D$	Dialdehyde $[\alpha]^{20}_D$	Dibasic acid $[\alpha]^{20}_D$	Strontium salt $[\alpha]^{20}_D$
α-Methyl-*d*-lyxoside	+59.4	+124.1	−12.8	−54.7
α-Methyl-*d*-arabinoside[4]	−17	+124.2	−12.7	−55.5
α-Methyl-*d*-xyloside[4]	+154	+125.2	−12.1	−55.5

The oxidation of the methyl-lyxopyranoside by periodic acid follows the reaction equation that has been found to hold for the xylose and arabinose methyl-pyranosides,[4] namely



Experimental

Oxidation of α-Methyl-*d*-lyxopyranoside with Periodic Acid.—To a solution of 1.3583 g. of pure α-methyl-*d*-lyxoside in 60 cc. of water was added 28.27 cc. of 0.615 *M* periodic acid solution (2.1 molecular equivalents). The solution was quickly diluted to 100 cc. and the rotatory changes observed at about 20°. From an initial specific rotation of +59.4° the rotation rapidly increased during the first ten minutes and became practically constant at the end of twenty-five minutes. After standing at 20° for twenty-one hours the solution had a specific rotation of +124.1° (referring to the dialdehyde). Five cubic centimeters of the solution was analyzed for periodic acid and the result showed that one mol of the lyxoside had consumed 1.988 mols of periodic acid, which conforms with the equation previously stated.

The free methoxy-diglycolic aldehyde (II) was obtained in a sirupy form by following the procedure used by Jackson and Hudson in the isolation of the dialdehyde resulting from the periodic acid oxidation of other methyl pentopyranosides. To the sirupy dialdehyde, dissolved in 330 cc. of water, 25 g. of strontium carbonate and 2 cc. of bromine were added and the mixture was shaken for five hours. After standing at room temperature for an additional eighteen hours the excess bromine was removed by aeration and the strontium carbonate by filtration. The bromide ions were removed by shaking with 17 g. of silver carbonate, the silver ions precipitated by hydrogen sulfide and the excess hydrogen sulfide removed by aeration. The solution was concentrated *in vacuo* in a bath at 60° to a volume of 10 cc., when crystallization of the strontium methoxy-diglycolate trihydrate commenced: yield, 1.8 g. (76%). Recrystallized three times from 8 parts of water the substance was obtained in the form of needle-like crystals exhibiting a rotation of −43.7° (*c*, 0.8; *l*, 4).

Anal. Calcd. for $C_5H_6O_6Sr \cdot 3H_2O$: C, 19.75; H, 3.98; OCH_3, 10.21; Sr, 28.85; H_2O, 17.79. Found: C, 19.86; H, 4.11; OCH_3, 10.14; Sr, 28.62; H_2O, 17.73.

Anhydrous strontium methoxy-diglycolate was obtained by heating the trihydrate at 100° *in vacuo* for four hours. Its solution in water gave a specific rotation of −54.7° (*c*, 1.2; *l*, 4).

Anal. Calcd. for $C_5H_6O_6Sr$: C, 24.03; H, 2.42. Found: C, 24.01; H, 2.61.

Summary

The oxidation of α-methyl-*d*-lyxoside by periodic acid yields a dialdehyde which, on oxidation by bromine water in the presence of excess strontium carbonate, forms the same crystalline strontium D′-methoxy diglycolate trihydrate (76% yield) that has previously been obtained from the α-methyl-pyranosides of *d*-arabinose and *d*-xylose. The result confirms the conclusion of Hirst and Smith from methylation data that the lyxoside is a pyranoside, and proves that it is an α-form.

WASHINGTON, D. C. RECEIVED JUNE 24, 1938

(5) I have expressed some years ago the view that the lyxoside is a furanoside because of a certain anomaly in its optical rotation [*ibid.*, **52**, 1689 (1930)] but the methylation data of Hirst and Smith[3] show that it is a pyranoside and their conclusion is now confirmed by the results of the periodic acid oxidation.—C. S. HUDSON.