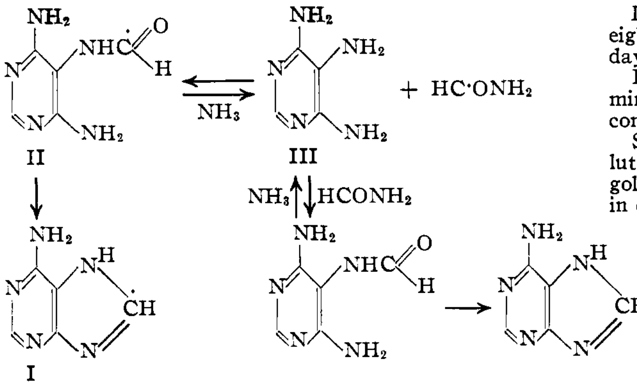

C* is C^{13}

Experimental

4,6-Diamino-5-formamidopyrimidine Sulfate[2] (II).—4,5,6-Triaminopyrimidine sulfate (III) (500 mg., 0.0022 mole) was warmed with 2 cc. of 25% aqueous formic acid, prepared by the hydrolysis of hydrogen cyanide.[5] (22.2 atom per cent. excess C^{13}) until all the solid had gone into solution. Upon cooling, 360 mg. (78%) of 4,6-diamino-5-formamidopyrimidine sulfate ($(C_5H_7ON_5)_2\cdot H_2SO_4\cdot H_2O$) separated. Isotope analysis showed 4.37 atom per cent. excess C^{13} (calcd. 4.44). The product was characterized by a comparison of its ultraviolet absorption spectrum with that of an authentic sample: $\epsilon_{max} = 4600$, $\lambda = 259$ mμ; authentic sample $\epsilon_{max} = 4690$, $\lambda = 259$ mμ.

Adenine Sulfate[2] (I).—(a) Compound II (345 mg.) was heated with 3 cc. of freshly distilled formamide for two and one-half hours at 165° in a sealed tube. On cooling the adenine which separated was recrystallized from 2 *N* sulfuric acid and contained 1.06 atom per cent. excess C^{13}, or about one-quarter of the expected value; yield, 280 mg., 70%.

Anal. Calcd. for $C_5H_5N_5\cdot H_2SO_4\cdot {}^1/_2H_2O$: N, 28.9, S, 13.2. Found: N, 28.7; S, 13.7.[6]

(b) Under the same conditions, 4,5,6-triaminopyrimidine sulfate resulted in a 62% yield of adenine sulfate.

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(5) Krieble and McNally, This Journal, **51**, 3368 (1929).

(6) Adenine is obtained as $(C_5H_5N_5)_2\cdot H_2SO_4\cdot H_2O$ if crystallization is rapid.

Sloan-Kettering Institute
for Cancer Research
New York 21, N. Y.
Received February 14, 1949

The Solution of Gold by Selenic Acid

By William E. Caldwell and Lowell P. Eddy

The solvent action of concentrated selenic acid at temperatures of 250° and over is known.[1] It has seemed to us worth while to ascertain the rapidity of this reaction at lower temperatures and in less concentrated solutions.

In the first experiments 50-mg. portions of flattened fine gold wire, 0.49 mm. in diameter, were sealed in three thick-walled Pyrex glass tubes with 0.5 ml. of 67, 87 and 98% selenic acid, respectively, and heated in the vapor of boiling chlorobenzene (130°). In the second experiments similar tubes were charged with 20 mg. of the gold in the same amount of the same acids and were heated in the vapor of boiling bromobenzene (154°).

In the most dilute acid at 130° no action was evident for thirteen days, and at 154° none for twenty-six days.

In the 87% acid at 130° some action was evident after eight hours and solution was complete after twenty-six days; at 154° solution was complete after thirteen days.

In the 98% acid at 130° dissolution began after ten minutes and was complete in three days; at 154° it was complete in thirteen hours.

Solutions of the gold in the concentrated acid when diluted with water yielded small golden-yellow crystals of gold selenate. These crystals were found to be insoluble in common organic solvents but in every case the crystals showed blackening, indicating oxidation of the organic material and reduction of the selenate.

Since both gold and selenium are used to color glass a pink or red, it was of interest to try use of powdered gold selenate for this purpose. A small quantity of glass was prepared by fusing two grams of sodium carbonate, one gram of calcium carbonate, four grams of silica, with a milligram of gold selenate. A lovely pink-violet glass resulted.

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(1) Lenher, This Journal, **24**, 354 (1902).

Oregon State College
Corvallis, Oregon
Received February 5, 1949

Molecular Properties of Water-soluble Polysaccharides from Western Larch

By Gerd Lystad Borgin[1]

Previous studies of the molecular properties of the water-soluble polysaccharides from larch (exact species, age and part of tree, sapwood and heartwood, not given) by Mosimann and Svedberg[3] using the sedimentation velocity ultracentrifuge technique indicate that the material consists of two components with molecular weights of 100,000 and 16,000.

Present studies were made on the extract from both the sapwood and the heartwood of a 30-year old butt log of Western larch. The water-soluble extract of the heartwood obtained at 30° was 8.4% of the wood and that of the sapwood was 0.9%. The pentosan content of the extracts was 13.7 and 11.9%, respectively.

The pentosan content of the single heartwood component, 13.7%, is within the range of the pentosan contents given by Peterson and collaborators[4] for three different types of larch, 13.1 to 14.3%. The pentosan content of the combined α- and β-constituents of the sapwood, 11.9%, is almost identical to the value given by Wise and Peterson,[5] 11.95%. Neither of these groups of investigators indicated what part of the wood was used. It is hence possible that Peterson and collaborators may have used heartwood and Wise and Peterson sapwood.

Sedimentation velocity runs showed the heart-

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(1) Foreign collaborator, Oslo, Norway. The author wishes to thank Drs. Alfred J. Stamm and Geo. J. Ritter of the Forest Products Laboratory[2] for making available the facilities of their laboratory and for suggestions in the chemical phase of the work and Prof. J. W. Williams of the Chemistry Department of the University of Wisconsin for making available the University's ultracentrifuge, which was used in this research.

(2) Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

(3) Mosimann and Svedberg, *Kolloid Z.*, **100**, 1 (1942).

(4) Peterson, Barry, Unkauf and Wise, This Journal, **62**, 2361 (1940).

(5) Wise and Peterson, *Ind. Eng. Chem.*, **22**, 362 (1930).

wood extract to be made up of one component with a sedimentation constant of 4.5×10^{-13} c.g.s. unit, whereas the sapwood extract was made up of two components with sedimentation constants of 4.5×10^{-13} and 1.2×10^{-13} c. g. s. unit (see Figs. 1 and 2). The two components were estimated to be present in the proportions of 3:2, the component of higher molecular weight being present in the larger amount. If the higher molecular weight component of both extracts is the same material, as appears to be the case, the calculated pentosan content of the higher molecular-weight component of the sapwood is 8.9%.

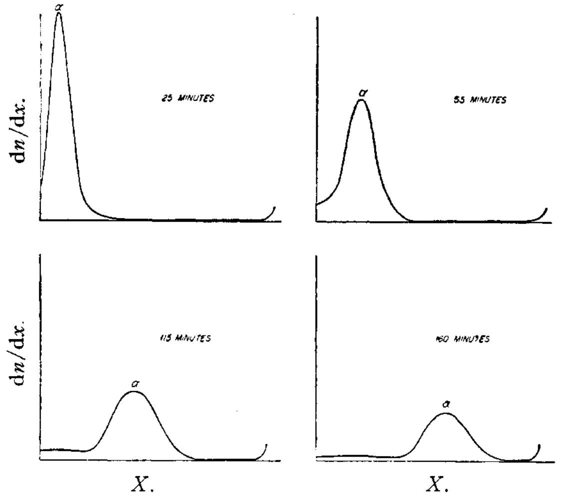

Fig. 1.—Sedimentation diagram of polysaccharide from the heartwood of Western larch at different times after the centrifuge had gained full speed: abscissa, distance from axis of rotation; ordinate, refractive index gradient; 25, 55, 115 and 160 minutes.

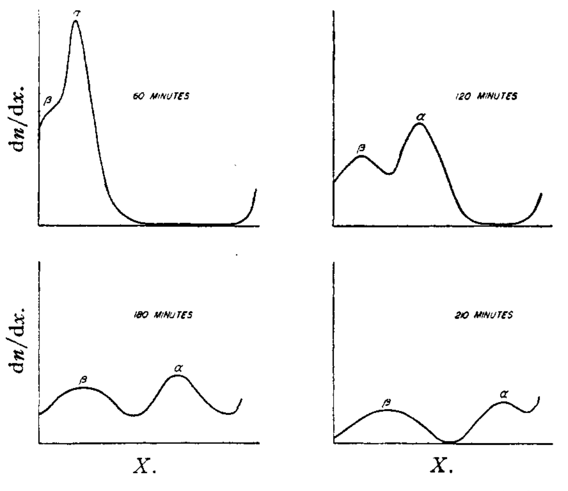

Fig. 2.—Sedimentation diagram of polysaccharide from the sapwood of Western larch at different times after the centrifuge had gained full speed: abscissa, distance from axis of rotation; ordinate, refractive index gradient; 60, 120, 180, and 210 minutes.

Forest Products Laboratory
Forest Service
U. S. Department of Agriculture
Madison, Wis.

Received December 3, 1948

Peracetic Acid Oxidation of Thiol Esters

By Chester J. Cavallito and Dorothy McKenica Fruehauf

The preparation of the thiolsulfinates by peracid oxidation of disulfides[1] suggested an attempt at preparation of α-keto sulfoxides and sulfones by a similar oxidation of thiol esters. Only one such compound, an aromatic α-ketosulfone, has been described briefly in the chemical literature.[2] Oxidation of thiol esters with peracetic or perbenzoic acids did not yield the α-keto sulfoxides or sulfones, but acid degradation products. The yields isolated are given in parentheses.

Peracetic acid in excess (6 moles to 1) in acetonitrile at 25° oxidized benzyl thiolbenzoate to two moles of benzoic acid (65%). Similarly, *p*-nitrobenzyl thiolbenzoate yielded *p*-nitrobenzoic (89%) and benzoic (95%) acids. Butyl thiolbenzoate gave benzoic acid (65%) and butanesulfonic acid (16%); the oxidative degradation did not proceed to the carbon atom of the aliphatic radical. Benzyl mercaptan yielded benzylsulfonic acid (93%); benzyl disulfide also gave the sulfonic acid with excess per-acid, but formed the thiolsulfonate as an intermediate. Benzyl benzoate was not oxidized under these conditions.

With one molar equivalent of per-acid, benzyl thiolbenzoate gave benzoic acid, (24% for two moles) considerable starting material (53%) and a trace of benzaldehyde. Benzyl thiolacetate yielded starting product (35%) and benzyl benzyl thiolsulfonate (40%); excess per acid converted the latter to benzylsulfonic acid.

The oxidation of RCH_2-S-COR′ therefore proceeds to R-COOH and R′COOH where R and R′ are aromatic; to RCH_2SO_3H and R′COOH where R is aliphatic or where R is aromatic and R′ is aliphatic. In the last instance, an intermediate is RCH_2SO_2SR, formed by either disproportionation of an intermediate α-keto sulfoxide or sulfone or from benzylsulfinic acid.[3] In the first type, RCH_2-SO-COR′ may be first formed and rearranges to RCHO and R′COSH, both of which react further with per-acid yielding RCOOH, R′COOH and SO_2.

Potassium permanganate or hydrogen peroxide in acetone did not oxidize the thiol esters at 25°. Otto and Lüders[4] obtained benzoic acid and benzylsulfonic acid from permanganate oxidation of benzyl thiolbenzoate in acetic acid.

(1) Small, Bailey and Cavallito, This Journal, **69**, 1710 (1947).
(2) Kohler and MacDonald, *Am. Chem. J.*, **22**, 219 (1899).
(3) Fromm and Palma, *Ber.*, **39**, 3310 (1906).
(4) Otto and Lüders, *ibid.*, **13**, 1285 (1880).