2. Cymylhydrazones of cinnamylaldehyde, salicylaldehyde and benzophenone were made. The hydrazones of methyl ethyl ketone, acetophenone and benzaldehyde were found to be unstable.
3. *p*-Cymyl-1-semicarbazide-2 and *p*-cymyl-1-thiosemicarbazide-2 were prepared.
4. A *p*-nitrobenzoyl derivative was prepared.
5. Cymylhydrazine reacts with carbon disulfide to give a product whose nature was not solved.

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[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY, FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE, IN COÖPERATION WITH THE UNIVERSITY OF WISCONSIN]

SEQUOYITE, A CYCLOSE FROM REDWOOD (SEQUOIA SEMPERVIRENS)

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RECEIVED JUNE 10, 1929 PUBLISHED OCTOBER 5, 1929

In a recent paper[3] we reported the isolation of a new cyclose which occurs with pinite in the cold-water extract of the heartwood of redwood. First analyses indicated that the new compound might have the empirical formula $C_8H_{16}O_7$, but later analyses upon purer and larger amounts of the material proved that it is a monomethyl ether of *i*-inosite and is isomeric with pinite, bornesite and quebrachite. The present paper describes the details of isolation, the experimental results that convinced us of its structural formula and the preparation of some of its derivatives.

Sequoyite, as we have named it, was isolated from the aqueous extract of redwood in a manner similar to that employed for pinite. The two cycloses crystallized out together upon the addition of alcohol to the thick, concentrated extract. They were separated from each other by fractional crystallization; sequoyite, being less soluble in either alcohol or water, crystallized readily from a 50% alcoholic solution, while the pinite crystallized slowly from a 70% solution.

The impure sequoyite crystals were purified by warming with a small amount of barium hydroxide, then filtering off the precipitated gums and coloring matter and acidifying the filtrate with sulfuric acid to remove the excess barium. The solution that remained after filtering off the barium sulfate was nearly colorless. The new cyclose was obtained from this solution by concentrating it to a thin sirup and then diluting it with

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[3] Sherrard and Kurth, *Ind. Eng. Chem.*, **20**, 722 (1928).

alcohol. The crystals were finally obtained in the pure state after recrystallization from alcohol and water.

The yield on the basis of the weight of the oven-dried heartwood varied from traces to 0.06%.

When pure, sequoyite crystallizes from alcohol and water in small transparent prisms which melt at 234–235° (uncorr.) and sublime at temperatures above this. It has a sweet taste, is readily soluble in water, is only slightly soluble in hot alcohol and is insoluble in ether, benzene or carbon tetrachloride. It is optically inactive, does not reduce Fehling's reagent, gives no precipitate with phenylhydrazine and is not affected by dilute acids or alkalies. When heated with nitric acid it is oxidized to oxalic acid. In cold, concentrated sulfuric acid it dissolves slowly without charring. It is not affected by acetic anhydride at room temperature.

Anal. Calcd. for $C_7H_{14}O_6$: C, 43.27; H, 7.27. Found: C, 43.11, 43.31, 43.20; H, 7.24, 7.30, 7.28. Calcd. for $C_6H_{11}O_5OCH_3$: OCH_3, 15.9. Found: OCH_3, 14.87, 15.3, 15.4. Determination of the molecular weight by cryoscopic methods gave 188 and 197.

Sequoyite Pentacetate.—The new cyclose was acetylated by boiling 1 g. of the pure crystals with an equal weight of anhydrous sodium acetate and 15 cc. of acetic anhydride for one hour in an oil-bath. Upon adding water to the cooled reaction mixture, the pentacetate separated out. It was recrystallized from hot alcohol.

Sequoyite pentacetate is obtained from hot alcohol in small, needle-like crystals which melt at 198° (uncorr.) and sublime at temperatures above this. It is also soluble in ether and is insoluble in water.

Anal. Calcd. for $C_6H_6(O_2C_2H_3)_5OCH_3$: C, 50.47; H, 5.98; CH_3CO, 53.22. Found: C, 50.26, 50.50; H, 5.86, 5.82; CH_3CO, 52.62, 52.78, 52.60.

The percentage of acetyl was determined by hydrolyzing the pentacetate with sodium hydroxide and also with barium hydroxide.

In hydrolyzing with sodium hydroxide, the acetylated compound was boiled for one-half hour with an excess of the *N*/10 alkali. It was then rapidly cooled, phenolphthalein was added and the amount of alkali required for hydrolysis was determined by titrating with standard acid.

In the barium hydroxide method the acetylated compound was boiled for two and a half hours in a reflux apparatus using a 1:1 solution of methyl alcohol and water as a solvent. The product was filtered, the filtrate was treated with carbonic anhydride in excess, was again filtered and the final filtrate was then evaporated. The residue was dissolved in water, the liquid was filtered and the barium in the filtrate was determined as sulfate. The original sequoyite was recovered by this method and retained a melting point of 235°.

From the hydriodic acid residue remaining from the methoxyl determinations, inactive inosite was obtained. It is formed when sequoyite is heated with hydriodic acid, reacting in accordance with the following equation:

$$C_6H_6(OH)_5OCH_3 + HI = C_6H_6(OH)_6 + CH_3I$$

It was separated from the reaction mixture by evaporating off the hydriodic acid in a steam-bath, dissolving the residue in a small amount of warm water and precipitating with alcohol. When recrystallized from alcohol and water it melted at 224° (corr.). The hexacetate derivative was prepared and it melted at 215° (corr.).

When 1.0688 g. of sequoyite was heated with hydriodic acid in a small distilling flask, 0.9192 g. or 86.0% of the sequoyite was recovered as *i*-inosite and a sufficient amount of the methyl iodide was collected for a boiling-point determination. It boiled between 43 and 44°. A maximum yield of 93.1% of the theoretical amount of *i*-inosite or 89.4% of the weight of the sequoyite was obtained from a hydriodic acid residue remaining from a methoxyl determination.

A careful investigation of the chemical literature indicates that no compound with the properties here described has been previously reported. We are therefore convinced that we have isolated a new cyclose. Since methyl iodide and *i*-inosite are the only decomposition products obtained and since they are obtained in the proportion corresponding to a compound having the molecular formula $C_6H_6(OH)_5OCH_3$, sequoyite must be a monomethyl ether of inactive inosite.

Summary

1. The isolation of a new cyclose from the heartwood of redwood has been described.
2. Experimental results show that this compound is a monomethyl ether of *i*-inosite.
3. Upon heating with hydriodic acid, two decomposition products are obtained and have been identified as methyl iodide and *i*-inosite.
4. The pentacetate derivative has been prepared and described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

1,2-BENZ-3,4-ANTHRAQUINONE

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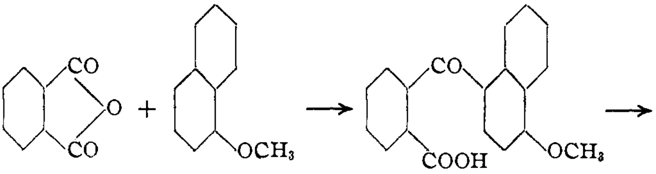
RECEIVED JUNE 10, 1929 PUBLISHED OCTOBER 5, 1929

In connection with a study of the reduction potentials of some of the higher benzologues of anthraquinone and phenanthrenequinone, we became interested in securing the compound named in the title. A suitable method of preparing the quinone was found in the oxidation of 4-amino-3-hydroxy-1,2-benzanthracene, which, in turn, was obtained from 3-hydroxy-1,2-benzanthracene.

The synthesis of the methyl ether of 3-hydroxy-1,2-benzanthracene, IV, was accomplished in the following manner



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