

solution maintained at 70–80° for 20–22 hours. When cold, the mixture was rendered alkaline with dilute ammonium hydroxide, extracted with ether and the ether distilled off. The residue obtained upon removal of the ethyl ether was treated at 60° for seven hours with a solution containing 220 g. of potassium hydroxide, 660 ml. of water and 2500 ml. of ethanol. The solution was then concentrated to approximately 750 ml. at 40° under reduced pressure. The resulting mixture was extracted with ether, the extracts washed with water and the ether removed. The product was purified by two recrystallizations from ethanol; white crystals, which sinter at 69° and melt 70–71° (cor.); yield 30–37 g. (55–67%). Hydroxylation of 50 g. of allyl *n*-octadecyl ether according to the procedure described by Davies, Heilbron and Owens⁴ gave only 19 g. (34%) of pure glyceryl ether.

Allyl Alcohol and Sodium Allyl Oxide.—A solution of sodium (45 g.) in allyl alcohol (700 cc., Eastman Kodak Co. white label quality) was protected by a soda-lime guard tube while it was refluxed gently for forty-eight hours. The turbid mixture was cooled, diluted with water and extracted thoroughly with ether. The aqueous alkaline solution was then acidified with sirupy phosphoric acid and again extracted with ether. In this way the product was separated into a neutral (A) and an acidic (B) fraction. The ether solutions were washed with water, dried and distilled at 2 mm. From (A) was obtained 66 g. of material boiling at 63–140° with n_D^{25} ranging from 1.4696 to 1.5148. (B) gave 90 g. of material boiling at 73–155° with n_D^{25} ranging from 1.4673 to 1.5021. In each instance the first portion of the distillate was colorless and very fluid; with rising boiling point the distillate gradually becomes light yellow and quite viscous. Both (A) and (B) were insoluble in water, but soluble in ethanol, and both gave negative fuchsin tests. Both absorbed hydrogen over Adams catalyst and gave positive tests for unsaturation with bromine in carbon tetrachloride. (A) reacted with sodium, evolving a gas.

This experiment was repeated several times with substantially the same results. In one run allyl alcohol which had been dried over Drierite was employed and the reaction carried out in an atmosphere of nitrogen with results essentially the same as those described above. Conversion of allyl alcohol to high boiling products under these conditions has apparently not been reported previously.

The neutral and acidic fractions were not investigated further.

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The Structure of Skita's "Decahydro-9,10-dihydroxyphenanthrene"

BY PHILIP LEVINE¹

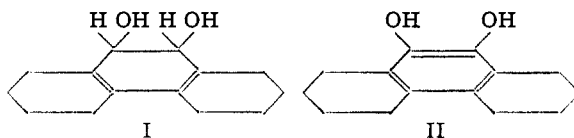
In a previous article,² reference was made to the preparation of a compound identical with that described by Skita³ as decahydro-9,10-dihydroxy-

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(2) Linstead and Levine, *THIS JOURNAL*, **64**, 2022 (1942).

(3) Skita, *Ber.*, **58**, 2685 (1925).

phenanthrene (I). Further investigation of this substance has now shown that the meso positions have not been hydrogenated and that the compound in question is *s*-octahydro-9,10-dihydroxyphenanthrene (II).



The reasons for questioning the structure proposed by Skita were the resistance of the compound to hydrogenation over Raney nickel at 120°, the failure to undergo dehydration to *s*-octahydro-9-phenanthrol, and the readiness with which the compound is oxidized by the atmosphere. Also Skita's only evidence for the glycol structure (I) was the analytical data for the compound itself and for its diacetate. A comparison of Skita's figures with the calculated values for (II) and its derivative shows that the analytical data do not suffice to distinguish between (I) and (II).

Oxidation of the compound to the octahydroquinone requires only one equivalent of lead tetraacetate. Assuming Skita's formula, one might expect either normal cleavage to the dialdehyde or the consumption of *two* equivalents of lead tetraacetate for oxidation to the quinone.

The question was unequivocally settled in favor of the hydroquinone structure (II) by reductive acetylation of the quinone obtained by oxidizing the compound. The diacetate thus obtained was identical in appearance and melting point with the diacetate from the original compound and no depression of the melting point was observed on mixing the two samples. The method used for the reductive acetylation of the quinone was that which normally converts a quinone into the diacetate of the corresponding hydroquinone without effecting any further reduction.

Experimental⁴

Lead Tetraacetate Oxidation of Octahydrophenanthrene-hydroquinone.—To 0.7 g. of the hydroquinone in 15 cc. of benzene was added in small portions 1.4 g. (one equivalent) of lead tetraacetate. The solution became deep red. Additional lead tetraacetate was unreacted as shown by tests with starch-iodide paper. A small amount of glycerol was added to remove excess oxidizing agent. The benzene solution was washed twice with water, dried over magnesium sulfate, and evaporated almost to dryness. The brilliant red crystals, melting at 139–141°, were evi-

(4) All melting points are corrected.

dently identical with the quinone obtained by Skita, m. p. 142°. Needles melting at 142–144° were obtained by crystallization from methanol.

Silver Oxide Oxidation of Octahydrophenanthrenehydroquinone.—A mixture of 0.42 g. of hydroquinone (m. p. 133–137°), 1 g. of silver oxide, and 1 g. of magnesium sulfate in absolute ether was shaken for one-half hour and filtered. The quinone proved to be soluble with difficulty in ether and was therefore extracted from the solids with benzene. Most of the benzene was evaporated and the product (0.338 g., m. p. about 137°) precipitated from the remaining solvent with hexane. Red needles melting at 142° were obtained by crystallization from acetone, which proved to be the best solvent for the purpose.

Reductive Acetylation of Octahydrophenanthraquinone.—Two drops of triethylamine was added to 0.1 g. of quinone with 0.1 g. of zinc dust in 2 cc. of acetic anhydride. The mixture was allowed to stand for ten minutes, heated to boiling, filtered, and the residue washed with hot acetic acid. Water was added to the boiling filtrate and washings to the cloud point. On cooling, the solution deposited 0.134 g. of white needles melting at 162–163°.

Acetylation of the Hydroquinone.—Addition of a drop of triethylamine to some of the hydroquinone (m. p. 135–137°) with a pinch of zinc dust in acetic anhydride caused slight warming. The mixture was allowed to stand a few hours and boiled for five minutes. The mixture was worked up in the same way as the product from the reductive acetylation of the quinone. The white needles melted at 161.5–163°. The mixed m. p. with the diacetate from the quinone was 162–163°.

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Atomic Weight of Lead from a Second Sample of Pitchblende, Great Bear Lake, N. W. T., Canada

BY JOHN PUTNAM MARBLE

In a continuation of the geochemical studies on the pitchblende ores of Great Bear Lake, the atomic weight of the lead in a second sample has been determined. This sample, from the 800-foot section of the No. 2 vein, Eldorado mine, Labine Point, Great Bear Lake, N. W. T., Canada, was received from H. S. Spence, Esq., of the Canada Department of Mines and Resources, for whose coöperation we are deeply grateful. The material is of the pitchblende-silica type ore, came from depth (below 100 feet), and carried no visible alteration products. Microscopic studies show a very small amount of galena, estimated at a fraction of one per cent.

The lead-uranium ratio uncorrected for "com-

mon lead," with an autoradiograph showing little evidence of alteration¹ and a complete analysis² have been previously published. While the results of this present work are admittedly incomplete, it was thought worth while to put them on record, as they are in virtual agreement with those of the first sample³ and the carrying out of further atomic weight determinations, or preferably of the determination of the isotope ratios of this sample, have necessarily had to be deferred. Since the pitchblende is virtually thorium-free, the atomic weight indicates the approximate correction to be made for "common lead," which cannot be done for thorium-rich minerals.

The preparation of the material for analysis, the extraction and purification of the lead, and the method of analysis were essentially the same as in the case of the first sample of Great Bear Lake lead.³ The work was done in the T. Jefferson Coolidge Memorial Laboratory of Chemistry at Harvard University, by kind permission of Dr. Gregory P. Baxter, for whose interest and assistance we are deeply grateful. The results of the analysis are as follows

Vac. wt. PbCl ₂	1.56541 g.
Vac. wt. Ag	1.21935 g.
Wt. Ag added in solution	0.00010 g.
Vac. wt. Ag ⇌ PbCl ₂	1.21945 g.
Ratio PbCl ₂ /2Ag	1.28370
Atomic weight Pb	206.057
(Ag = 107.880; Cl = 35.457)	

This value agrees so closely with that of the work on the earlier sample (Pb = 206.054), that we may conclude that the lead in the Great Bear Lake pitchblende ore shows no appreciable variation in isotopic composition in different parts of the deposit, and also that a correction of about 4 per cent. should be applied to the "uncorrected" lead-uranium ratio of the second analyzed sample, as was done for the first. Further work may confirm these conclusions.

(1) J. P. Marble, *Am. Mineralogist*, **22**, 564 (1937).

(2) J. P. Marble, *ibid.*, **24**, 272 (1939).

(3) J. P. Marble, *THIS JOURNAL*, **56**, 854 (1934).

U. S. NATIONAL MUSEUM
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Saponins and Sapogenins. XX. Some Color Reactions of Triterpenoid Sapogenins

BY C. R. NOLLER, R. A. SMITH, G. H. HARRIS AND J. W. WALKER

While attempting to prepare the acid chlorides of some triterpenoid acids by means of thionyl