

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°.

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY RECEIVED SEPTEMBER 24, 1942
CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE COMMITTEE ON MEASUREMENT OF GEOLOGIC TIME, DIVISION OF GEOLOGY AND GEOGRAPHY, NATIONAL RESEARCH COUNCIL]

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
WASHINGTON, D. C.

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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

chloride, it was noted that one of two commercial preparations of thionyl chloride caused the formation of highly colored solutions, for example burgundy red with echinocystic acid and a brilliant blue with hederagenin, while the other lot gave only colorless, yellow or red solutions. When the first lot of thionyl chloride was purified by the usual procedure over quinoline and linseed oil, it no longer gave the brilliant colors. Fractional distillation using a packed column gave no appreciable separation of the impurity. Accordingly a systematic qualitative analysis was made of the impure sample. This indicated a considerable amount of tin to be present, some iron and a trace of phosphorus. Quantitative analysis showed amounts equivalent to 0.007% stannic chloride, 0.004% ferric chloride and less than 0.001% phosphorus. When a solution of 0.01% of anhydrous stannic chloride and 0.005% of sublimed ferric chloride in purified thionyl chloride was allowed to react with various triterpenoids, the colors produced by the impure thionyl chloride were practically duplicated. Differences may be attributed to traces of phosphoric acid in the commercial sample.

Pure stannic chloride dissolved in pure thionyl chloride produced characteristic colors but stannic chloride dissolved in benzene, petroleum ether, ethyl ether, carbon tetrachloride, chloroform or cyclohexane was without effect. Ferric chloride, antimony trichloride, antimony pentachloride, phosphoric acid, or phosphorus oxychloride which has been exposed to moisture, and concentrated sulfuric acid in thionyl chloride produced colors but purified phosphorus oxychloride, phosphorus trichloride, phosphorus pentachloride, silicon tetrachloride, chlorine, sulfur dioxide and hydrogen chloride, when dissolved in thionyl chloride, do not give a color-producing reagent.

The colors produced vary with the reagent and with the compound used. Sometimes a sequence of colors is produced, which may be so rapid at first that the solution must be observed continuously in order to note them. Usually the color changes are complete after an hour although sometimes they are not complete after twenty-four hours. In the case of the hydroxy acids, the intense colors are produced only if at least one free hydroxyl group is present; if all the hydroxyl groups are esterified the intensity of the colors is greatly decreased. Esterification of the carboxyl group is without effect. In the case of the α - and

β -amyryns, which lack a carboxyl group, the intensity of the colors is little changed by esterification. Differences between isomeric compounds, for example echinocystic acid and hederagenin, or α -amyryn and β -amyryn, may be sufficiently great to distinguish readily between them.

Little can be said concerning the cause of the colors. The inorganic compounds producing the color all may be considered as electron accepting reagents but we see no reason why stannic chloride should be effective only in thionyl chloride solution and not in other anhydrous solvents. The colored compounds might be looked upon as halochromic salts but the intensity and brilliance of the colors, particularly the blues and purples with stannic chloride, would seem to call for a chromophoric group with greater possibilities of resonance than are afforded by a single unconjugated carbon-carbon double bond, a carboxyl group and two hydroxyl groups.¹

The color changes produced on treating 0.02 g. each of a wide variety of triterpenoids and their derivatives with 0.5 cc. of 0.01% anhydrous stannic chloride in pure thionyl chloride in a small test-tube which was kept stoppered during observation, may be summarized as follows:

Hederagenin, light pink \rightarrow violet \rightarrow light blue \rightarrow deep orange after one hour.

Hederagenin methyl ester, pink \rightarrow purple \rightarrow violet \rightarrow deep yellow after eight hours.

Hederagenin diacetate, light yellow \rightarrow yellow after eight hours.

Echinocystic acid, pink \rightarrow purple \rightarrow blue \rightarrow light red \rightarrow very deep red after twenty-four hours.

Methyl echinocystate, red \rightarrow blue-green \rightarrow purple \rightarrow very deep red after one hour.

Echinocystic acid diacetate, colorless \rightarrow light violet \rightarrow light orange after twenty-four hours.

Methyl echinocystate diacetate, colorless \rightarrow light violet \rightarrow deep yellow after twenty-four hours.

Echinocystic acid monoacetate (by esterification), pink \rightarrow violet \rightarrow deep blue \rightarrow red after two hours.

Echinocystic acid monoacetate (by hydrolysis), violet \rightarrow deep green \rightarrow very deep red after twenty minutes.

Isonorechinocystenedione, yellow \rightarrow orange \rightarrow red after twenty-four hours.

Ursolic acid, light pink \rightarrow deep red \rightarrow light red \rightarrow very deep red after eight hours.

Oleanolic acid, light pink \rightarrow very deep red after one hour.

Methyl oleanolate, light pink \rightarrow very deep red after one hour.

Methyl oleanolate acetate, light yellow \rightarrow light violet \rightarrow deep yellow after twenty-four hours.

Betulic acid, colorless \rightarrow light violet \rightarrow dark muddy green after one hour.

(1) One of the referees states, "There is no question but that we are dealing here with some very complex adsorption reactions."

α -Amyrin, orange \rightarrow very deep red \rightarrow very deep purple after twenty-four hours.

β -Amyrin, purple \rightarrow very deep red after five minutes.

α -Amyrin benzoate, light pink \rightarrow deep red after one hour.

β -Amyrin benzoate, light yellow \rightarrow red \rightarrow deep yellow \rightarrow orange after twenty-four hours.

α -Amyrone, colorless \rightarrow yellow \rightarrow orange after twenty-four hours.

β -Amyrone, colorless \rightarrow light blue \rightarrow purple \rightarrow deep red after eight hours.

The color changes of a limited group of triterpenoids with (A) pure thionyl chloride, (B) 0.01% anhydrous ferric chloride in thionyl chloride, (C) 0.01% antimony trichloride in thionyl chloride, (D) 0.01% antimony pentachloride in thionyl chloride, (E) 10% phosphorus oxychloride + 0.5% water in thionyl chloride, (F) 0.01% stannic chloride + 0.005% ferric chloride in thionyl chloride and (G) commercial thionyl chloride may be summarized as follows:

Hederagenin, (A) colorless \rightarrow light amber (B) orange \rightarrow red \rightarrow green \rightarrow amber (C) orange \rightarrow violet \rightarrow blue \rightarrow green \rightarrow red \rightarrow brown (D) yellow \rightarrow red \rightarrow green \rightarrow yellow \rightarrow orange (E) blue \rightarrow green \rightarrow orange \rightarrow red (F) violet \rightarrow purple \rightarrow blue \rightarrow green \rightarrow amber (G) red \rightarrow blue \rightarrow green \rightarrow amber.

Echinocystic acid, (A) colorless \rightarrow pink \rightarrow red (B) orange \rightarrow red \rightarrow violet \rightarrow red (C) pink \rightarrow violet \rightarrow blue-green \rightarrow red (D) pink \rightarrow violet \rightarrow blue \rightarrow violet \rightarrow red (E) violet \rightarrow blue-green \rightarrow violet \rightarrow red (F) red \rightarrow purple \rightarrow blue-green \rightarrow red (G) violet \rightarrow blue \rightarrow blue-green \rightarrow red.

Oleanolic acid, (A) pink \rightarrow violet \rightarrow red (B) violet \rightarrow purple \rightarrow red (C) violet \rightarrow red (D) violet \rightarrow blue \rightarrow red (E) pink \rightarrow red (F) violet \rightarrow red (G) violet \rightarrow purple \rightarrow red.

Ursolic acid, (A) yellow \rightarrow orange \rightarrow red (B) violet \rightarrow purple \rightarrow red (C) violet \rightarrow red (D) yellow \rightarrow orange \rightarrow red (E) orange \rightarrow red (F) red (G) violet \rightarrow blue \rightarrow purple \rightarrow red.

α -Amyrin, (A) pink \rightarrow purple \rightarrow red (B) orange \rightarrow red (C) yellow \rightarrow orange \rightarrow red (D) yellow \rightarrow red (E) colorless \rightarrow yellow \rightarrow orange \rightarrow red (F) yellow \rightarrow red (G) red.

β -Amyrin (A) colorless \rightarrow pink \rightarrow violet \rightarrow red (C) purple \rightarrow blue \rightarrow red (D) red \rightarrow blue \rightarrow purple \rightarrow red (E) blue \rightarrow opaque.

Betulin, (A) colorless \rightarrow yellow \rightarrow green (F) yellow \rightarrow red \rightarrow purple \rightarrow green (G) yellow \rightarrow red \rightarrow purple \rightarrow green.

STANFORD UNIVERSITY
STANFORD UNIV., CALIF.

RECEIVED JUNE 15, 1942

Peroxides in Isopropanol

By C. ERNST REDEMANN

While it is a widely known fact that ethyl ether, isopropyl ether, and dioxane readily form peroxides when stored in contact with air or oxygen, there seems to be no mention of the formation

of peroxides in isopropanol when stored under similar conditions.

A sample of 99.5% isopropanol, which had been stored for many months in strong daylight in a clear glass bottle only about one-third filled, was observed to have a strong unpleasant odor. Since this odor greatly resembled the odor of isopropyl ether when it is badly contaminated with peroxides, the isopropanol was investigated for the presence of peroxides. The following tests for peroxides were strongly positive: (1) immediate liberation of iodine from acidified potassium iodide solution, (2) the formation of blue peroxychromic acid, soluble in ether, from chromic acid solutions, (3) the production of chemiluminescence from 3-amino-phthalhydrazide catalyzed by hemoglobin,¹ (4) precipitation of Prussian blue from a solution containing ferric chloride and potassium ferricyanide,² (5) reduction of black nickel oxide to pale green nickelous hydroxide,³ (6) decolorization of lead sulfide.⁴

Quantitative iodometric determinations were made of the peroxide content of all samples of isopropanol available in this Laboratory with the results shown in the table.

Sample	Peroxide, mole/l.	Conditions of storage
1	0.36	Clear glass bottle, $\frac{1}{3}$ full, strong light
2	.13	Clear glass bottle, $\frac{2}{3}$ full, strong light
3	.04	Clear glass bottle, $\frac{5}{8}$ full, strong light
4	.05	Clear glass bottle, $\frac{5}{8}$ full, strong light
5	.003	Tin can, nearly full, dark
6	.007	Redistilled, stored about four years, largely in the dark

This reaction appears, in part, to be a photochemical process. The following brief experiment was designed to indicate the comparatively rapid rate of formation of peroxide in strong light. Twenty-five ml. of isopropanol was placed in a 500-ml. Pyrex glass flask fitted with a capillary tube to equalize external and internal pressure. The flask was left on the roof in full daylight for two days. Initial peroxide content 0.003 mole/l.; after two days 0.026 mole/l.

These data are presented to call the attention of experimenters to the need for making sure that isopropanol is peroxide free when working with easily oxidizable material. Likewise, some care should be exercised when evaporating old isopropanol solutions to dryness as an explosion

(1) Schales, *Ber.*, **72**, 167 (1939).

(2) Schönbein, *J. prakt. Chem.*, [1] **79**, 67 (1859).

(3) Feigl and Fränkel, *Mikrochemie*, **13**, 304 (1932/1933).

(4) Kempf, *Z. anal. Chem.*, **89**, 88 (1933).