TABLE I

SOLUBILITY AND DENSITY DATA AT 20°

NaOH, moles/liter	KI, moles/liter	Density, g./ml.
0.00	6.09	1.716
0.95	5.48	1.674
1.34	5.26	1.661
2.57	4.58	1.624
3.60	4.06	1.597
4.77	3.53	1.573
5.04	3.44	1.568
5.20	3.35	1.564
6.78	2.75	1.543
7.77	2.42	1.532
8.68	2.18	1.531
10.06	1.81	1.526
10.80	1.67	1.530
13.45	1.29	1.540
16.22	1.03	1.569
16.50	1.03	1.583

rapidly than with potassium iodide in potassium hydroxide solutions. The solid phase in equilibrium with solution 16.22 *N* in alkali was washed free from solution and dried. Analysis of the crystals gave 76.07% iodine (calcd. for KI 76.45%). The crystals were optically isotropic.

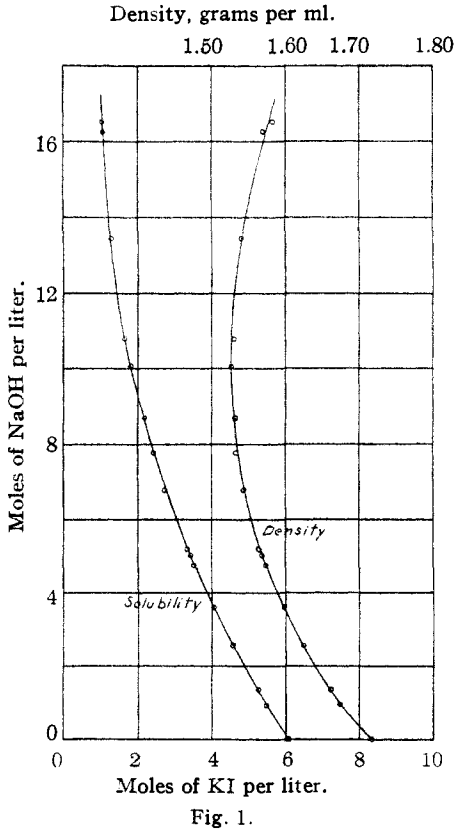

Fig. 1.

These observations, and the apparent continuity of the curves, indicate that potassium iodide was the only solid iodine compound in equilibrium with the solutions. The accuracy of the results is estimated to be 0.5%.

CONTRIBUTION FROM THE
CHEMISTRY LABORATORY
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Isolation of Quercitrin and Quercetin from Goldenrod Material

BY JOHN D. GUTHRIE, ROBERT T. O'CONNOR, MACK F. STANSBURY AND THEODORE R. SAVICH

Quercitrin (3,3′,4′,5,7-pentahydroxyflavone-3-rhamnoside) and its aglucone, quercetin, were isolated from the acetone extractives of goldenrod, *Solidago leavenworthii*, T. and G. Since 15 to 20% of the dry goldenrod material, chiefly leaves, was soluble in acetone, a large quantity of material was available as a by-product from the acetone–benzene extraction process for obtaining rubber from goldenrod.

Experimental

Quercitrin.—Goldenrod leaf material that had been dried in a tray drier at 65° was ground to pass a 40-mesh screen, extracted with acetone in a Soxhlet-type metal extractor for forty-eight hours and the acetone removed from the extract by distillation. Quercitrin was isolated by extraction of the green, gummy material with 0.25 *N* sodium hydroxide, acidification of the extract with acetic acid, centrifugation, neutralization of the supernatant liquid with sodium hydroxide solution and precipitation of the quercitrin with lead acetate. After decomposition of the lead precipitate with hydrogen sulfide, some of the quercitrin was found in the filtrate and some adsorbed on the lead sulfide precipitate, from which it could be eluted with acetone. The quercitrin was purified by crystallization from dilute acetone. In a typical experiment 1.7 g. was obtained from 25 g. of the acetone-extractives. A solution in 95% ethanol had absorption maxima at 2600 and 3500 Å.

Anal. Calcd. for quercitrin, dry, $C_{21}H_{20}O_{11}$: C, 56.3; H, 4.7. Found after drying *in vacuo* at 170°, C, 56.2; H, 4.5.

The aglucone was obtained by hydrolysis of the quercitrin. Its absorption maxima were at 2560 and 3720 Å. in 95% ethanol.

Anal. Calcd. for quercetin, $C_{15}H_{10}O_7$: C, 59.6; H, 3.3. Found: C, 59.1; H, 3.4.

The hydrolyzate gave the Rosenthaler test for rhamnose and yielded the osazone of rhamnose. After recrystallization from dilute pyridine and dilute methanol, it melted at 184–185° (cor.); mixed melting point 184–185° (cor.). Nitrogen: found, 16.33; calcd., 16.36.

Quercetin.—Goldenrod leaf material that had been dried at 65° was extracted in a large jacketed extractor by percolation with acetone at 50° for twenty-four to thirty-six hours. After recovery of the acetone by distillation, the extractives were melted by heating to about 140° and poured into cans. Quercetin was isolated from 47 kg. of the green, gummy acetone-extractives by extraction with boiling water, hydrolysis of the quercitrin in the hot water extract by adding sulfuric acid in the amount of 1% and heating. The crude product which separated weighed 4.3 kg. and contained about 58% quercetin. It was purified by solution in alcohol, precipitation with water, recrystallization from 80% alcohol, and fractional precipitation from acetone with petroleum ether. The yield of purified quercetin was 780 g.

Anal. Calcd. for $C_{15}H_{10}O_7$: C, 59.6; H, 3.3. Found: after drying at 170° *in vacuo*, C, 59.2; H, 3.8.

The pentaacetate was prepared and melted at 200° (cor.). The mixed melting point with a known sample of the pentaacetate of quercetin was 200° (cor.). Sando gives 194 to 196° for the melting point of the pentaacetate of quercetin.[1] The absorption curves of the two samples of the pentaacetate in 95% ethanol were practically identical. The absorption maxima were at 2530 and 2990 A. with extinction coefficients (*E*, g. per liter, 1 cm.) of 40.0 and 34.5, respectively. Quercetin was regenerated from the pentaacetate preparations. The absorption curves of the regenerated quercetin preparations in 95% ethanol were practically identical. The maxima were at 2570 and 3750 Å. with extinction coefficients of 67.0 and 75.5, respectively, calculated on the dry basis. Grinbaumówna and Marchlewski give 2555 and 3755 Å. for the absorption maxima of quercetin.[2]

The micro-analyses were made by G. Warren Buckaloo and Lawrence E. Brown.

(1) C. E. Sando, *J. Biol. Chem.*, **117**, 45 (1937).

(2) R. Grinbaumówna and L. Marchlewski, *Biochem. Z.*, **290**, 261 (1937).

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Observations on the Rare Earths. LII. The Preparation of Rare Earth Bromates from the Perchlorates

BY HOWARD E. KREMERS[1] AND THERALD MOELLER

In the preparation of rare earth bromates by metathetical reaction between rare earth sulfates and barium bromate,[2] significant quantities of rare earth materials are occluded by the precipitated barium sulfate. Furthermore, the method is complicated by the limited solubility of barium bromate.[2] Reactions between rare earth perchlorates and the more soluble potassium bromate overcome these objections, the precipitated potassium perchlorate showing less tendency to occlude rare earth salts than barium sulfate because of its somewhat greater solubility and consequent slower rate of precipitation. Bromates are also more readily prepared in this fashion than by treatment of rare earth oxides or hydroxides with bromic acid and are suited to fractional crystallization.

Experimental

Nearly neutral rare earth perchlorate solutions, prepared from yttrium group oxides by action with perchloric acid and containing the equivalent of 15 to 20% rare earth oxide, were treated with powdered potassium bromate and the resulting mixtures boiled for one hour. After being cooled to 15°, the suspensions were filtered and the residues washed with saturated potassium perchlorate solution until the washings were rare earth-free. These precipitates generally contained about 0.1% rare earth calculated as oxide, and never more than 0.5%.

Each filtrate was systematically fractionally crystallized to six fractions after fifteen crystallizations. Analyses of these fractions by standard methods showed the most insoluble fractions to consist of potassium bromate with traces of potassium perchlorate, the middle fractions to consist of rare earth bromates with traces of potassium bromate, and the most soluble fractions to consist of rare earth bromates with traces of rare earth perchlorates.

During the course of the fractionation, small amounts of potassium perchlorate and basic rare earth bromates precipitated. The latter never amounted to more than 1% of the total fraction, and such precipitations did not prove objectionable.

The preparation of rare earth bromates from perchlorates is more convenient and rapid than the preparation involving barium bromate, but the removal of by-products is not as complete. Since potassium bromate and perchlorate rapidly concentrate in the most insoluble fractions while remaining traces of perchlorate are carried through to the most soluble fractions, fractional crystallization is not impaired. Avoidance of loss of rare earth material in the initial precipitation constitutes the chief recommendation for the method.

(1) Present address, Lindsay Light and Chemical Company, West Chicago, Illinois.

(2) James, THIS JOURNAL, **30**, 182 (1908).

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Sterols from Peruvian Guano

BY JOHN KRUEGER

The sterol present in comparatively large amounts in Peruvian guano and provisionally called "guanosterol" or "guanosterine"[1] is really cholesterol as shown by the m. p. and m. m. p. of both the sterol and its acetate. Marker[2] has shown that the sterol present in largest amount in chicken feces is sitosterol. The cholesterol present in guano reflects the diet of the marine birds which produce the deposits.

Procedure.—Three pounds of Peruvian guano was stirred with 4 liters of ethanol at 40–50° for several hours, and the mixture then allowed to stand overnight. The residue was filtered and the filtrate was evaporated. The residue from the evaporation was refluxed with excess alcoholic sodium hydroxide, diluted with water, then extracted into ether. The pale tan sterol obtained by evaporation of the washed ether solution was recrystallized from 30 cc. of ethanol to yield 4.0 g. of cholesterol of m. p. 142° which showed no depression in m. m. p. when mixed with cholesterol. The acetate, prepared in the usual way, melted at 113° and showed no depression in m. m. p. when mixed with cholesteryl acetate.

(1) del Aguila, *Bol. soc. Quim. Peru*, **4**, 199–200 (1938) (*C. A.*, **33**, 2270 (1939)).

(2) Marker and Shabica, THIS JOURNAL, **62**, 2523 (1940).

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Electrophoresis of Rat Sera[1]

BY CHOH HAO LI

In the last few years, many investigators[2] have studied the electrophoresis of animal and human sera, but apparently no studies with rat sera have

(1) Aided by grants from the University of California Research Board, the Josiah Macy, Jr., Foundation, New York City, and General Mills, Inc., Minneapolis, Minnesota.

(2) Referred to, for example, by H. Svenson, *J. Biol. Chem.*, **139**, 805 (1941).