cate needles is obtained, m.p. 165–168°. After recrystallization from ether–chloroform the m.p. is 172–174°. *Anal.* Calcd. for $C_{31}H_{47}O_6Cl$: C, 67.55; H, 8.59. Found: C 67.53; H, 8.80.

Dehalogenation.—A solution of 500 mg. of 5-chlorokryptogenin diacetate in 5 cc. of glacial acetic acid and 500 mg. of anhydrous potassium acetate is refluxed for one hour. After cooling, the reaction product is poured into water and extracted with ether. The residue left by evaporation of the ethereal solution is crystallized from ethanol, m.p. 147–150°. This product gave no depression with an authentic sample of kryptogenin diacetate.

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MÉXICO, D. F.
RECEIVED JANUARY 30, 1948

Separation of Radium from Barium by the Use of an Ion-exchange Column Procedure[1]

BY EDWARD R. TOMPKINS[2]

In current radium production processes, the radium and barium are separated by fractional crystallization, the method originally developed by the Curie's. This is a very tedious process, which requires many recrystallizations and extensive recycling of the various fractions to obtain a clean separation without excessive losses. To carry out this procedure without endangering the safety of the operating personnel requires considerable remote control equipment, and, because of the large number of operations, contributes appreciably to the present cost of radium.

In the course of extensive investigations of ion-exchange separation methods for the preparation of pure fission products,[3] it was noted that microgram quantities of strontium and barium (two of the fission elements) could be separated readily by this method. The separation, which depends chiefly upon the differences in the dissociation constants of the barium and strontium citrate complexes, was made by first adsorbing the mixture at the top of a bed of synthetic ion-exchange resin, Amberlite IR-1, 100 cm. in length, and subsequently eluting the elements preferentially from this column by the use of complexing agents at carefully adjusted values of *p*H. By exercising considerable care it was possible to effect nearly complete separation of the barium and strontium in these low concentrations, although the separation was much poorer when milligram quantities of these elements were present. The apparatus was simple and was thus easily adaptable to remote control procedures.

Recently samples of several new organic exchangers have been obtained.[4] One of these, Dowex 50, has a much higher combining capacity than any exchanger tested here previously. Because of this it is much more applicable to the separation of ponderable quantities of materials. Extensive studies of this resin for rare earth separations[5,6,7] had shown the importance of using small particle sizes and/or elevated temperature to obtain optimum results. A special sample of colloidal agglomerates of Dowex 50 had proved especially effective for rare earth separations, a column of this resin 10 cm. in length giving a better separation than had been obtained with a 100-cm. column of Amberlite resin under similar conditions.[6]

From these results and the earlier observations regarding the behavior of strontium and barium when eluted from Amberlite resin columns, it appeared that a good separation of barium from radium should be possible by the use of a short column of the new resin. Because of the much greater affinity of Dowex 50 resin for cations (as compared to IR-1), it was necessary to determine the correct conditions for the elution of the alkaline earths from this resin. Whereas the separation with IR-1 had been made by eluting strontium and barium with 0.23 *M* citrate at *p*H 4.75, preliminary experiments with strontium showed that it was necessary to use 0.5 *M* citrate at *p*H 7.5 to 8.0 to remove it from Dowex 50 at a convenient rate. It was also shown that barium and strontium in trace concentrations could be separated by elution from a column of colloidal agglomerates of Dowex 50, 1 sq. cm. × 15 cm.

This column of colloidal agglomerates was next employed to test the separation of barium from radium. The starting solution containing $20\mu c$ ($20\ \mu g$) of radium, 20 mg. of barium with Ba^{140} tracer (and La^{140} daughter) and 20 mg. of strontium with $Sr^{89,90}$ tracer, was first slowly passed through the column, causing the solute mixture to be adsorbed at the top. Ammonium citrate solution, 0.5 *M* (*p*H 7.8), was then passed through the column at a rate of 0.3 ml. per minute, the effluent being monitored by means of a special apparatus consisting of a thin-windowed flow cell facing a mica-windowed Geiger–Mueller counter tube which was attached to a counting rate meter and recorder. By means of this apparatus it was possible to obtain a continuous record of the concentration of the β- and γ-emitters in the effluent from the column. A reproduction of this recorded curve is shown by the solid, curved line in Fig. 1.

Fractions of the effluent solution were collected as indicated on this curve (I to XVIII), and aliquots were counted for α, β and γ activity. Aluminum absorption and decay curves of these radioactivities were taken, as a method of determining the composition of each fraction. From these results the approximate composition of the various fractions and the percentage of each element

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[1] This work was done at Clinton Laboratories (renamed Oak Ridge National Laboratory), a part of the Plutonium Project, during June, 1947, and was done under Contract W-35-058-eng-71 for the Atomic Energy Project.

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[3] E. R. Tompkins, J. X. Khym and W. E. Cohn, THIS JOURNAL, **69**, 2769 (1947).

[4] Through the courtesy of W. C. Baumann, The Dow Chemical Company, Midland, Michigan.

[5] D. H. Harris and E. R. Tompkins, THIS JOURNAL, **69**, 2792 (1947).

[6] S. W. Mayer and E. R. Tompkins, *ibid.*, **69**, 2859, 2866 (1947).

[7] B. H. Ketelle and G. E. Boyd, *ibid.*, **69**, 2800 (1947).

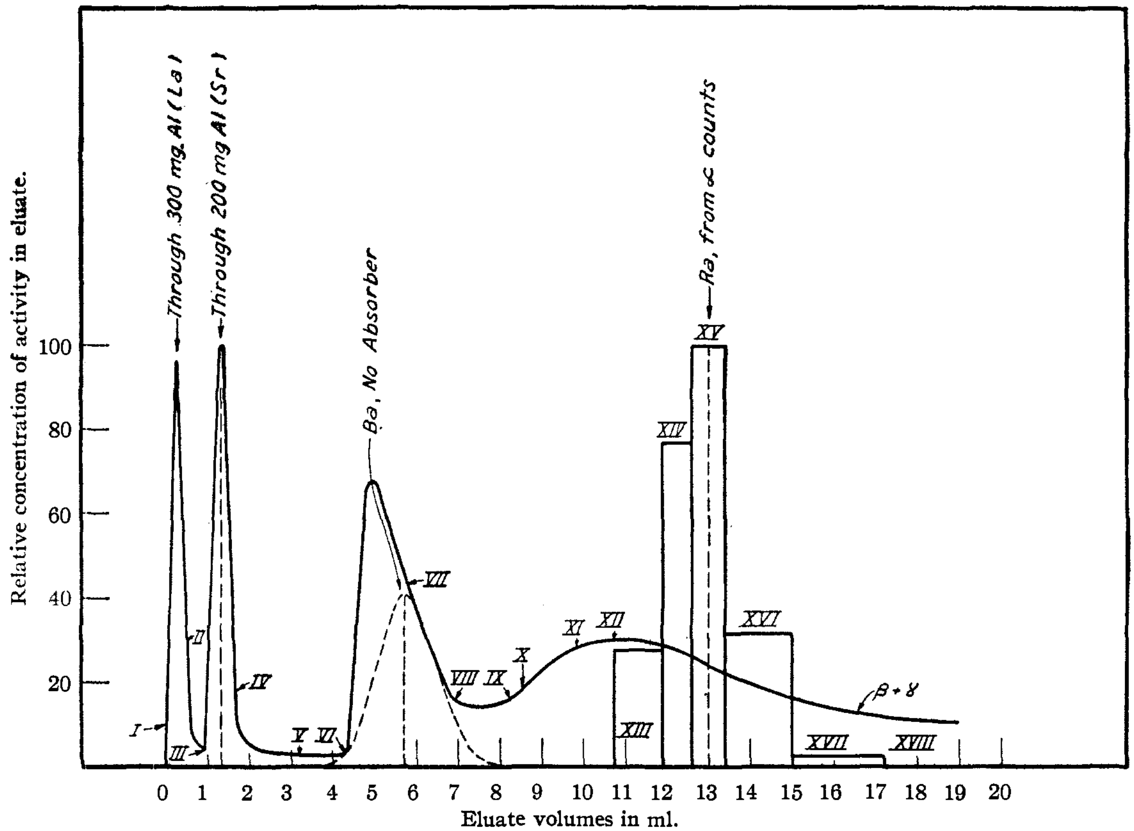

Fig. 1.—Separation of strontium, barium and radium.

in each of the various fractions were calculated. Table I summarizes this data.

TABLE I

COMPOSITION OF ELUATE FRACTIONS FROM SEPARATIONS COLUMN

Fraction	Per cent. of total				Percentage composition of fractions				
	La	Sr	Ba	Ra	La	Sr	Ba	Ra	Ra decay products
I	16.7	2.9	..		88	12	..	..	
II	75.0	4.4	..		97	3	..	..	
III	1.1	6.3	..		6	94	..	..	
IV	0.0	78.5	..		..	100	..	..	
V	1.0	7.8	..		14	96	..	..	
VI	0.4	0.1	..		82	18	..	..	
VII	5.8	..	82.5		27	...	73	..	
VIII	..	..	15.9		..	...	86	..	14
IX	..	..	1.6		..	...	50	..	50
X	..	..	..	..	..	...	..	..	100
XI	..	..	..	..	..	...	..	..	100
XII	..	..	..	..	..	...	..	..	100
XIII	..	..	..	9.4				100	
XIV	..	..	..	24.8				100	
XV	..	..	..	40.6				100	
XVI	..	..	..	22.5				100	
XVII	..	..	..	2.6				100	
XVIII	..	..	..	0.1				100	

In making the column run, the flow of elutrient solution was stopped overnight (seventeen hours) after fraction VI had been collected. This allowed the La^{140} daughter of the Ba^{140} (which was still adsorbed on the column) to grow back to about 20% saturation, thus affecting the shape of the recorded elution curve for the barium. Because the energy of the radiation from the daughter element is greater than that from the barium, the effect was accentuated in the recorded curve. The estimated elution curve for barium is shown by the broken curved line. The β and γ emitters in fractions X to XII inclusive decayed with a half-life of several hours (radium decay products), indicating that no detectable barium was present in these fractions.

From Table I it can be seen that the separation of strontium and barium and of barium and radium was nearly complete. (The failure of the recorded curve to fall to zero in the zone between strontium and barium is due to the continuous elution of La^{140} which was formed by the decay of Ba^{140} on the column.) Radium was detected by its α-activity. Sample XII showed the first α activity, but it decayed rapidly to a very low count, showing that it was chiefly radium decay products. The radium elution curve is shown graphically in Fig. 1, where radium concentration in the eluate (in arbitrary units) is plotted *versus* the eluate volume. It will be noted that essentially all the radium was contained in samples XIII to XVII, inclusive.

The results of this investigation indicate that the separation of radium from barium on a commercial basis could be much more easily effected by this column method than by the current procedure based on fractional crystallization. The method is simple to operate and thus may be easily adapted to remote control. The use of this separation method for the quantitative analysis of radium has not been investigated, but it is probably applicable.

OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE
RECEIVED MAY 24, 1948

NEW COMPOUNDS

1-(4-Chloromercuriphenylazo)-naphthol-2

This substance, synthesized in an effort to obtain a colored compound capable of attachment to biological tissue through mercaptan groups only, has been applied successfully in biological investigations.[1,2]

Synthesis.—35.4 g. of *p*-aminophenylmercuric acetate (m. p. 166–167°), prepared by direct mercuration of aniline according to the method of Dimroth,[3] was diazotized at −5° in 500 ml. of 50% acetic acid with 7.0 g. of sodium nitrite, according to the method of Jacobs and Heidelberger.[4] The filtered diazonium salt was coupled to 2-naphthol (15 g. of 2-naphthol, 180 g. of sodium hydroxide, in 2 l. of iced water). After standing a few hours, the precipitate was collected by filtration, washed, dissolved in 200 ml. of glacial acetic acid, filtered, and precipitated by dilution to 2 l. This precipitate was collected, washed, and dissolved by refluxing with 3 l. of 60% ethanol in a water-bath. The hot solution was filtered, the clear filtrate was brought to a boil under reflux, and to it was added 5.8 g. sodium chloride in 150 ml. of 60% ethanol. A cottony red precipitate of 1-(4-chloromercuriphenylazo)-naphthol-2 formed immediately. Refluxing was continued for thirty minutes, the precipitate, 3.6 g. (6.2%), collected by hot filtration and washed several times with boiling 50% ethanol. The precipitate was recrystallized three times from *n*-butyl alcohol (0.9 g. per l. of boiling alcohol) with 95% yield of fine red needle-like crystals which were virtually insoluble in water, but slightly soluble in cold alcohols, chloroform, toluene and decahydronaphthalene, melting with blackening at 291.5–293° (cor.).

Anal. Calcd. for $C_{16}H_{11}ClHgN_2O$: C, 39.76; H, 2.29; Cl, 7.34; Hg, 41.5; N, 5.80. Found: C, 39.36; H, 2.24; Cl, 7.12; Hg, 42.0; N, 6.01.[5]

Degradation.—The product was split by sodium hydrosulfite, yielding 1-amino-2-hydroxynaphthalene.

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[1] Bennett, *Anat. Rec.*, **100**, (suppl.) 7, 100 (1948).

[2] Bennett, in press.

[3] Dimroth, *Ber.*, **35**, 2032 (1902).

[4] Jacobs and Heidelberger, *J. Biol. Chem.*, **20**, 513 (1915).

[5] The analyses were preformed by Mr. Nagy of the Microchemical Lab., Massachusetts Institute of Technology.

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RECEIVED MAY 19, 1948

β-Glyceryl Phenyl Ether and 1,3-Dichloro-2-phenoxypropane

These compounds were prepared as intermediates in an effort, which proved unsuccessful, to synthesize phenyl cyclopropyl ether by the procedure described by Krantz and Drake[1] for the synthesis of methyl cyclopropyl ether.

β-Glyceryl Phenyl Ether.—The reduction of phenoxymalonic ester[2] by lithium aluminum hydride,[3] with alkaline hydrolysis of the intermediate aluminate, furnished the crude product, m. p. 59–66° in 95% yield. On recrystallization from benzene it was obtained as colorless needles, m. p. 68°. *Anal.*[4] Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.07; H, 7.19.

1,3-Dichloro-2-phenoxypropane. A. From β-Glyceryl Phenyl Ether and Thionyl Chloride.—A solution of 40 g. of β-glyceryl phenyl ether in 40 g. of pyridine, dissolved with the aid of heat, was added dropwise, keeping the temperature below 20°, to 200 g. of thionyl chloride. The flask, with reflux condenser attached, was heated very gently to start the evolution of sulfur dioxide and eventually more strongly until the temperature of the vapor in the flask reached 70°. Excess thionyl chloride was removed under reduced pressure. Water was then cautiously added to the residue, the mixture extracted with ether and the extract washed once with dilute alkali. The final purification was by fractional distillation under reduced pressure, using a 30″ wire-spiral column which resulted in a 75% yield of 1,3-dichloro-2-phenoxypropane, b. p. 103.5–104° (1 mm.), $n^{25}D$ 1.5358. *Anal.* Calcd. for $C_9H_{10}OCl_2$: C, 52.76; H, 4.92; Cl, 34.58. Found: C, 52.67; H, 5.15; Cl, 34.57.

B. From Benzene Diazonium Chloride and 1,3-Dichloropropan-2-ol.—Dry benzene diazonium chloride[5] prepared from 22 g. of aniline hydrochloride was added in small portions over a period of one-half hour, keeping the temperature below 25°, to 200 g. of redistilled 1,3-dichloropropan-2-ol (b. p. 173–175°). Stirring was continued until the evolution of nitrogen and hydrogen chloride ceased (about seventeen hours). Most of the excess dichloropropanol was removed by distillation at 10 mm. pressure and the residue was then fractionated at a lower pressure using the 30″ column. The yield of the desired product was 5.8 g., b. p. 99.5–100° (0.5 mm.), $n^{26}D$ 1.5369. *Anal.* Found: C, 53.20; H, 4.92; Cl, 34.27. The ultraviolet absorption spectrum, exhibiting a maximum at 270 mμ, was virtually identical with that of material prepared by Method A.

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RECEIVED JUNE 14, 1948

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[1] Krantz and Drake, U. S. Patent 2,330,979.

[2] Niederl and Roth, THIS JOURNAL, **62**, 1154 (1940).

[3] Nystrom and Brown, *ibid.*, **69**, 1197 (1947).

[4] Performed by Wm. Saschek.

[5] Pray, *J. Phys. Chem.*, **30**, 1478 (1926).

[6] Present address: Department of Chemistry, University of California at Los Angeles.

γ-Chlorocrotylmercaptoacetic Acid and γ-Chlorocrotylmercaptomethylpenicillin

One hundred thirty-five grams of 1,3-dichloro-2-butene (du Pont, Organic Chemicals Department) was added to a solution of 85 g. of sodium hydroxide and 108 g. of mercaptoacetic acid (85%) in 1.0 liter of water over a period of two hours. Rapid mechanical stirring was used and the mixture was held at 45–50° during the addition of the halide and for four hours thereafter. The mixture was extracted with ethylene dichloride and the aqueous layer was acidified with concentrated hydrochloric acid. The resulting oil was extracted with ethylene dichloride. After removal of the solvent the residual liquid was vacuum distilled. The main fraction boiled at 108–111° (0.6 mm.) and was a yellow liquid with a pronounced skunk-like odor; yield 128 g. (77%).

Anal. Calcd. for $C_6H_9ClO_2S$: C, 39.89; H, 5.02; neut. eq., 180.7. Found: C, 39.91; H, 5.04; neut. eq., 180.6.