TABLE I

	Product,[a] methyl *p*-carbomethoxy-	Varying component	Re-fluxing time (hr.)	M.p., °C.	Yield, %	Analyses Sapon. equiv. Calcd.	Analyses Sapon. equiv. Found	Analyses Calcd., % C	Analyses Calcd., % H	Analyses Found, % C	Analyses Found, % H
1	Phenoxyacetate	Methyl α-chloroacetate	15	93.6–94.5	63.9	112.1	112.4	58.92	5.39	58.75	5.38
2	Phenoxybutyrate	Methyl γ-chlorobutyrate	40	48.8–49.8	21.0	126.1	127.5	61.94	6.35	...	..
3	Phenoxyvalerate	Methyl δ-chlorovalerate	78	48.0–49.0	52.9	133.1	133.6	63.14	6.81	63.21	6.83
4	Phenoxycaproate	Methyl ε-chlorocaproate	82	44.6–45.4	52	140.2	141.0	64.27	7.19	64.35	7.10
5	Phenoxyheptanoate	Methyl ω-bromoheptanoate	39	54.2–55.3	20	147.2	147.2	65.29	7.53	65.33	7.44
6	Phenoxyundecanoate	Methyl 11-bromoundecanoate	24	69.0–70.0	91.5	175.2	175.6	68.57	8.57	...	..

[a] All products were crystallized from methyl alcohol–water; however, where unreacted methyl *p*-hydroxybenzoate was present, it was removed by washing a benzene solution of the product with aqueous NaOH.

Freshly cut sodium (33.1 g., 1.44 moles) was gradually introduced into 600 ml. of dry methanol in a two-liter flask equipped with a stirrer, reflux condenser with a drying tube, and dropping funnel. Upon complete solution of the sodium, first, 219.1 g. (1.44 moles) of methyl *p*-hydroxybenzoate in 400 ml. of methanol and later 217.6 g. (1.44 moles) of methyl δ-chlorovalerate were added rapidly. The reaction mixture was refluxed for a total of 78 hours during which time the newly formed sodium chloride was filtered away several times as a means of determining the end of reaction. Upon pouring the cooled reaction mixture into ice-water, a white lustrous precipitate settled out. The product after recrystallization from methyl alcohol–water contained a small amount of a slightly higher melting impurity (assumed to be unreacted methyl *p*-hydroxybenzoate) which was removed by washing a benzene solution of the precipitate with aqueous sodium hydroxide. Physical data pertaining to this compound as well as to the other dimethyl esters are found in Table I.

Intermediates necessary to the preparation of these esters were made according to methods found in literature. The following references were employed: for methyl γ-chlorobutyrate,[2] methyl ε-chlorocaproate,[2] methyl ω-bromoheptanoate[3] and methyl 11-bromoundecanoate.[4,5]

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(3) C. F. H. Allen, ref. 2, Coll. Vol. 1, 1941, p. 156.

(4) Conrad, *Ann.*, **188**, 218 (1877).

(5) R. Ashton and J. C. Smith, *J. Chem. Soc.*, 435 (1934).

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Ethyl 3β-Acetoxy-5,17(20)-pregnadiene-21-thiolate

BY ROGER W. JEANLOZ[1]

In a study of reductive desulfuration with Raney nickel, ethyl 3β-acetoxy-5,17(20)-pregnadiene-21-thiolate has been prepared directly from 3β,17β-diacetoxy-5-androstene-17α-acetic acid[2] and from 3β-acetoxy-5,17(20)-pregnadiene-21-ic acid.

3β-Acetoxy-5,17(20)-pregnadiene-21-ic Acid.—By the use of acetic acid and pyridine, 150 mg. of 3β-hydroxy-5,17(20)-pregnadiene-21-ic acid was acetylated. The product was crystallized from ether and gave 165 mg. (93%) of prisms, melting at 135–137°; $[\alpha]^{20}\text{D}$ −74° (*c*, 1.04 in chloroform).[3]

Anal. Calcd. for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66. Found: C, 74.10; H, 8.69.

Ethyl 3β-Acetoxy-5,17(20)-pregnadiene-21-thiolate.—Thionyl chloride (1.5 ml.) was added at 0° to 270 mg. of dry 3β,17β-diacetoxy-5-androstene-17α-acetic acid (m.p. 200°)[1] and kept at 0° for 12 hours with exclusion of moisture. The excess thionyl chloride was evaporated and the last traces removed by addition of absolute benzene and evaporation at reduced pressure. The crystalline acid chloride (not isolated) was dissolved in 2 ml. of absolute benzene and, after addition of 0.3 ml. of ethyl mercaptan and 0.1 ml. of absolute pyridine, was kept at room temperature for two days. The solution was then diluted with a small amount of water and extracted with ether. The extract was washed with dilute hydrochloric acid, sodium carbonate and water and dried over anhydrous sodium sulfate. The ethereal solution was decolorized with charcoal, evaporated to dryness and the residue, recrystallized from ether–pentane, yielded 255 mg. (95%) of colorless prismatic needles, m.p. 154–155°; $[\alpha]^{20}\text{D}$ −65° (*c*, 1.38 in chloroform).

Anal. Calcd. for $C_{25}H_{36}O_3S$: C, 72.07; H, 8.71; S, 7.70. Found: C, 71.57; H, 9.15; S, 7.84.

One hundred and twenty-five milligrams of 3β-acetoxy-5,17(20)-pregnadiene-21-ic acid was treated with thionyl chloride and then with ethyl mercaptan, as described above for 3β,17β-diacetoxy-5-androstene-17α-acetic acid. There was obtained 130 mg. (90%), melting at 150–152° (mixed m.p. with the specimen described above, 151–154°).

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(1) Worcester Foundation for Experimental Biology, Shrewsbury, Massachusetts.

(2) T. Reichstein, H. Müller, Ch. Meystre and M. Sutter, *Helv. Chim. Acta*, **22**, 741 (1939); Pl. A. Plattner and W. Schreck, *ibid.*, **22**, 1178 (1939).

(3) The melting points were determined on the Kofler micro melting point apparatus and the rotations observed in a 1-dm. tube of 0.8-ml. capacity.

Further Studies of the Ion-Exchange Separation of the Rare Earths[1]

BY B. H. KETELLE AND G. E. BOYD

Recently Higgins and Street[2] have called attention to the mislabelling of the Tb activity peak in our Fig. 6c which reported on the ion-exchange column separation of all fourteen of the trivalent rare earths using citrate buffers at 100°.[3] Partly reported[4a,b] further work in the Tb–Gd–Eu region conducted at this Laboratory in 1948 and 1949 has revealed not only this mistake, in agreement with Higgins and Street, but has shown also that the peak marked Y in Fig. 6c was actually Dy.

Before discussing our later ion-exchange separations, the reasons for these misidentifications, which we take this occasion to correct, may be of interest: The earlier assignment of the activity peak in Fig. 6c occurring at 2400 minutes to Y was based partly upon the argument that after such a time dysprosium activity (assumed to be 145 m Dy^{165}) would not have been detectable, and partly

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(1) This document is based on work performed under Contract Number W-7405 eng 26 for the Atomic Energy Project at Oak Ridge National Laboratory.

(2) G. H. Higgins and K. Street, THIS JOURNAL, **72**, 5321 (1950).

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

(4) (a) B. H. Ketelle, *Phys. Rev.*, **76**, 1256 (1949). (b) See private communication K(101) by B. H. Ketelle (Dec. 1948) to G. T. Seaborg concerning the decay sequence 3.6 m Gd^{161} → 7.0 d Tb^{161} reported in a Table of Isotopes by G. T. Seaborg and I. Perlman, *Rev. Mod. Phys.*, **20**, 585 (1948).

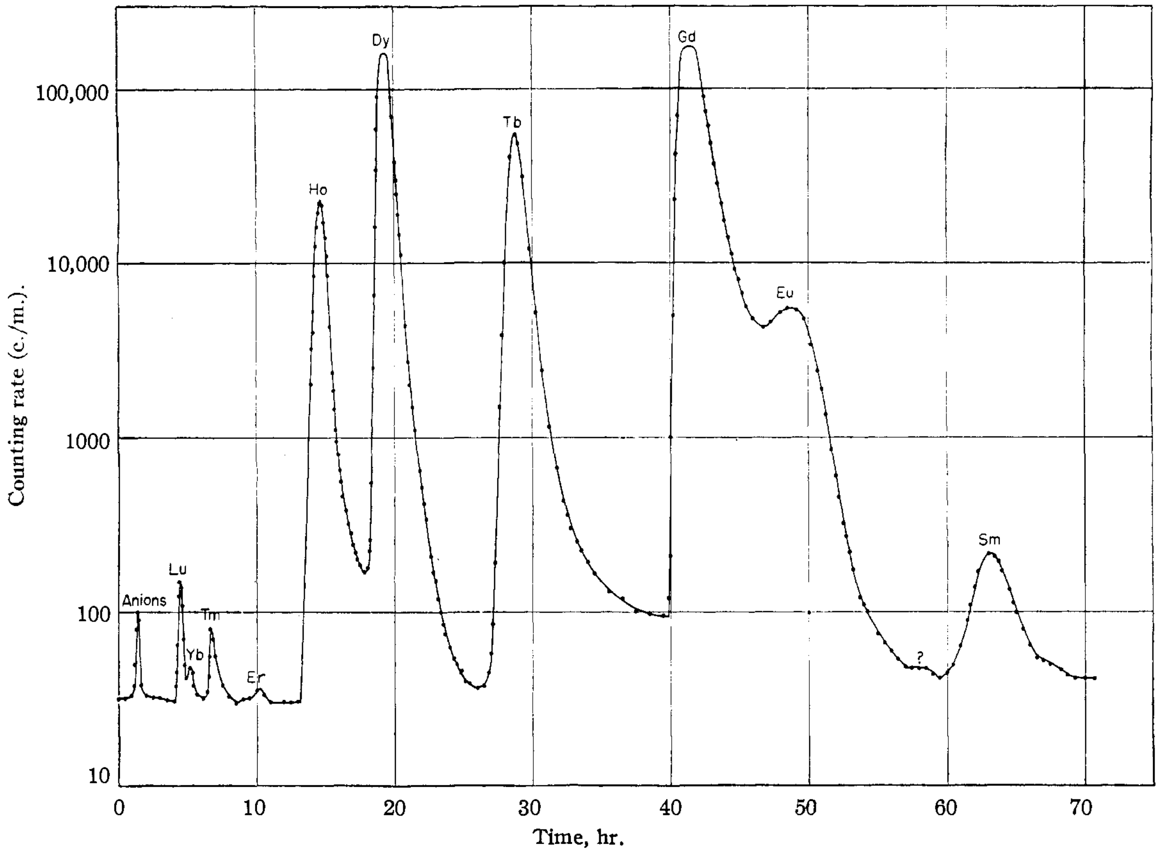

Fig. 1.—Yttrium earth separations effected with a 97 cm. column of 270/325 mesh Dowex 50 at 100° using 5% citrate buffer (*p*H 3.28) at a flow rate of 0.64 cm./min.; bed area 0.26 cm.^{2} Rare earth radioactivities produced by neutron irradiation of 2 mg. of Gd_2O_3, 0.2 mg. of Dy_2O_3 and 1 μg. of Eu_2O_3. Samarium activity peak from impurity in Eu; Tb peak from decay of 3.6 m Gd^{161}; Lu, Yb, Tm, Er and Ho peaks from impurities in Dy.

upon the observation that the decay period (81 h) for the activity peak in question corresponded to the approximately known value of 65 h for Y^{90} which was assumed to have been formed by neutron capture by a small yttrium impurity present in the irradiated Dy_2O_3. It has since been found[4a] that a second dysprosium activity, 81 h Dy^{166}, is formed in high yield by double neutron capture in stable dysprosium thus making possible the occurrence of a dysprosium activity peak in Fig. 6c.

The assignment of the activity peak at 3550 minutes to Gd was based upon the observation that a 7.0 d period was always produced in good yield in the neutron irradiation of Gd_2O_3 preparations of the highest purity. It has since been demonstrated[4b] that in actuality the 7.0 d activity belongs to Tb^{161} formed as a daughter of 3.6 m Gd^{161} which is the primary neutron capture product.

By reason of the change in *p*H of the eluting citrate buffer at 4550 minutes, the relative separations of Tb, Gd, Eu and Sm shown in Fig. 6c were distorted. Accordingly, this variable was maintained constant in order to determine the true relative separabilities in this region in our subsequent experiments. A typical separation of the yttrium group rare earths from Gd, Eu and Sm effected with a 0.26 sq. cm. by 97 cm. 270/325 mesh Dowex-50 column at 100° using citrate buffer (*p*H 3.28) at a flow rate of 0.64 cm./min. is illustrated by Fig. 1. These separations are believed to be superior to our previous efforts (see Figs. 6c and 6d, ref. 3) in that an almost complete separation of Eu and Sm was achieved. It is believed that the better resolution of the rare earths shown in Fig. 1 compared with that of Higgins and Street is due to the greater length of our column (*i.e.*, 97 compared with 20 cm.). The differences in the separability between Gd and its neighbors of lower and higher atomic number are shown clearly. In particular, the increased separation which occurred between Tb and Gd compared with that between Gd and Eu is of special interest in that it gives added weight to our earlier correlation[3] of the variations in the ion-exchange column separations of the trivalent lanthanides with the variations in their crystal radii. In fact, pursuant of the analogy between the trivalent actinides and lanthanides, it was predicted[5] that the ion-exchange column separation of element 97 (Bk), (analog of Tb) from Cm (analog of Gd) would be considerably easier than the separation of Cm from Am (analog of Eu). Interestingly, this expectation has been realized within recent months.[6]

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(5) G. E. Boyd, Lecture 29. "Isotopes and Chemistry of the Heavy Elements," Reactor Training School, ORNL, March 17, 1947).

(6) S. G. Thompson, B. B. Cunningham and G. T. Seaborg, THIS JOURNAL, **72**, 2798 (1950).