It is very possible that the high activity of Raney nickel is not only due to the large surface area of the catalyst but also to the presence of aluminum oxide; Ipatieff[3] has already demonstrated the pronounced effect of alumina upon a nickel catalyst.

Experimental Part

Samples of freshly prepared W-6 Raney nickel were introduced into weighed ampoules. Special precautions were taken not to expose the catalyst to the air and to have it covered with absolute ethanol during the transfer of the sample into the ampoules. The ampoules were then attached to an interchangeable joint which was sealed to the high vacuum line. The alcohol was removed under high vacuum; this evacuation was done gradually in order to avoid any bumping of the alcohol and splashing of the catalyst into the upper part of the ampoules. Best results were achieved by cooling the ampoules to about −78° and then raising the temperature slowly to about 40–50°. After all the alcohol was removed the ampoule was sealed off under vacuum at the upper restriction and weighed. The weight was determined to the nearest milligram. Each ampoule contained about one gram of the catalyst.

The ampoules were opened in the absence of air and treated with 100 ml. of 9% of nitric acid. On boiling, the nickel dissolved leaving a dense white residue. After cooling, 10 ml. of concd. sulfuric acid was added and the solution was boiled till all the residue dissolved. The clear solution was then transferred to 500-ml. volumetric flask and made to volume.

Nickel was determined on $^1/_{20}$th aliquots by precipitation as nickel dimethylglyoxime[4a] and weighed as such: The amount of aluminum present was established on $^1/_{10}$ aliquots by precipitation as basic succinate[5] followed by filtration and ignition to oxide at 1200°. Sodium was determined on $^1/_{10}$ aliquots by precipitation as sodium magnesium uranyl acetate.[4b]

In all determinations aliquots of two separate samples were used. The results obtained are summarized in Table I.

TABLE I

ANALYSIS OF W-6 RANEY NICKEL

	Sample 1	Sample 2	Average
Nickel	77.00	76.95	76.97
Aluminum	12.75	12.69	12.72
Sodium	0.15	0.15	0.15
Total	89.90	89.79	89.84

On the basis of the above data, the calculation reveals the following percentage composition of the W-6 Raney nickel: metallic nickel, 76.97; aluminum oxide, 21.13; sodium aluminate, 0.54; metallic aluminum, 1.36.

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(3) V. N. Ipatieff, *Ber.*, **45**, 3205 (1912).

(4) "Scott's Standard Methods of Chemical Analysis," N. H. Furman, Editor, 5th edition, Vol. I, D. Van Nostrand Company, Inc., New York, N. Y., 1939 (a) p. 619, (b) p. 879.

(5) H. H. Willard and N. K. Tang, *Ind. Eng. Chem., Anal. Ed.*, **9**, 357 (1937).

THE IPATIEFF HIGH PRESSURE AND
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RECEIVED JUNE 14, 1950

Note on the Ion Exchange Separation of Europium, Gadolinium and Terbium

BY G. H. HIGGINS AND K. STREET, JR.

In connection with the general problem of comparing the behavior of the actinide elements with their rare earth homologs, it was desirable to know the relative rates of elution of the rare earth triad europium, gadolinium and terbium on eluting with citrate solutions from Dowex-50 cation resin. Ketelle and Boyd[1] in Fig. 6c show an elution (run at 100°) of the heavy rare earth elements from Dowex-50 cation resin using 5% ammonium citrate solution of *p*H 3.25. In their experiment the activity peak that eluted in about 0.7 the time required to elute their europium peak is labeled Gd thus implying a large separation between europium and gadolinium. B. B. Cunningham and H. G. Hicks[2] ran europium and gadolinium under somewhat different conditions (room temperature and *p*H 3.05 citrate) and found practically no separation of europium and gadolinium. In addition, J. O. Rasmussen[3] ran europium, gadolinium and terbium under still different conditions (75° and *p*H 3.2 citrate) and again found essentially no separation of europium and gadolinium. In addition, he found that terbium was eluted well ahead of europium and gadolinium. It thus appeared that there was a real discrepancy between this later work and that of Ketelle and Boyd.

In order to check this point a run was made under conditions very close to those used by Ketelle and Boyd. Figure 1 shows the results of an elution of yttrium, terbium, gadolinium and europium made at 97° using 5% ammonium citrate solution of *p*H 3.25. Tracer Y^{91}, $Gd^{<154}$ and $Eu^{152-154}$ were used and in addition approximately

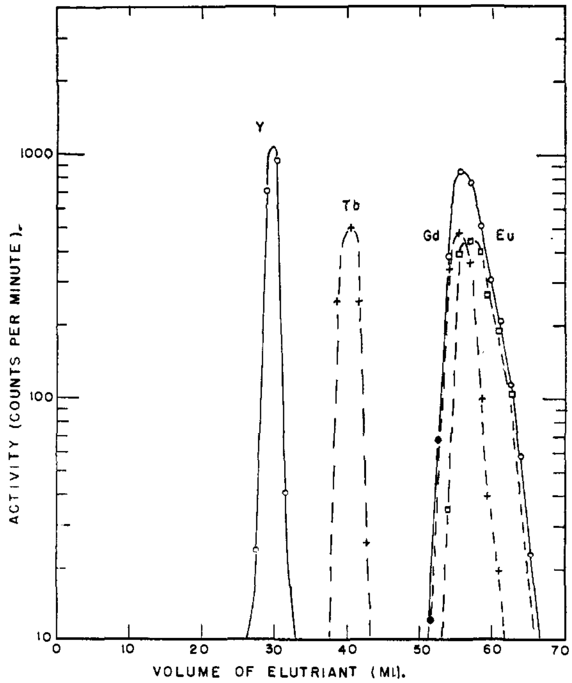

Fig. 1.—Elution of Y, Tb, Gd and Eu with *p*H 3.25 ammonium citrate at 97°.

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(1) B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947).

(2) B. B. Cunningham and H. G. Hicks, unpublished work.

(3) J. O. Rasmussen, unpublished work.

200-μg. amounts of stable terbium, gadolinium and europium were added to make spectrographic identification of the peaks possible. The column used was 20 cm. long and 5 mm. in diameter and a flow rate of 0.3 ml./sq. cm./min. was maintained. The Eu and Gd activities appear as a single broad peak; however, spectrographic analyses make possible the construction of the dashed curves for Eu, Gd and Tb. It is evident on comparing this elution with Fig. 6c of ref. 1 that the activity labeled Gd by Ketelle and Boyd is very likely a terbium activity and that any gadolinium activities they may have had are under the front of the europium peak.

It should be noted that the very small separation of gadolinium from europium and the much greater separation of terbium from gadolinium agrees very well with the expected effect of the half-filled 4f electron configuration as was first pointed out by Boyd.[1]

This work was performed under the auspices of the U. S. Atomic Energy Commission.

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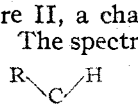
The Stereochemical Configuration of the Δ^{22}-Ergostenyl Side Chain

BY R. NORMAN JONES

Althouch the chemical structures of ergosterol and its photo-irradiation products have been known for several years, the stereochemical configuration of the substituents about the Δ^{22}-bond has not been fully established. From a study of the X-ray diffraction pattern of calciferol 4-iodo-5-nitrobenzoate, Crowfoot and Dunitz[1] have assigned a *trans* configuration to the C_{22} and C_{23} hydrogen atoms, and it is the purpose of this communication to draw attention to certain features of the infrared absorption spectra of steroids containing the Δ^{22}-ergostenyl side chain which confirm this structure.

Sutherland and co-workers[2] have observed that the out-of-plane deformation modes of vibration of the olefinic hydrogen atoms in the *trans*-ethylene structure I give rise to a strong absorption band near 965 cm.$^{-1}$, whereas in the *cis*-ethylene structure II, a characteristic band occurs at 690 cm.$^{-1}$. The spectra of several steroids containing the Δ^{22}-ergostenyl side chain have recently been measured in this Laboratory, and in all cases a prominent band is observed at 974–970 cm.$^{-1}$. This band is lacking from the spectra of the corresponding 22,23-dihydro derivatives and from the spectra of analogous compounds containing the cholestanyl side chain.



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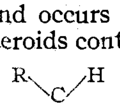


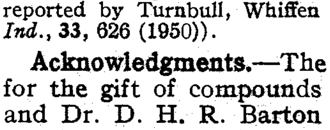
II

An example is provided by the spectra of ergostane and Δ^{22}-ergostene shown in Fig. 1. A band at the position designated A in Fig. 1 is observed also in the spectra of ergosterol, ergosteryl acetate, lumisteryl acetate and calciferol, all of which contain a Δ^{22}-ergostenyl side chain, but it is lacking from the spectra of Δ^{14}-ergostene, ergostanol-3β, ergostanyl acetate, cholestane, Δ^{5}-cholestene, cholesterol, cholestenyl acetate, 7-dehydrocholesterol, 7-dehydrocholestenyl acetate and vitamin D_3 which do not contain this group. The 974–970 cm.$^{-1}$ band must be distinguished carefully from a weaker band, designated B in Fig. 1, which is observed at 962–958 cm.$^{-1}$ in most of the above compounds. None of the Δ^{22}-ergostenyl derivatives possess any bands of significant intensity between 700 and 680 cm.$^{-1}$.

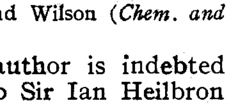
It is therefore to be inferred that the 974–970 cm.$^{-1}$ band is associated with the presence of the Δ^{22}-double bond in the molecule which must possess the *trans* configuration.

The olefins listed in the A.P.I. "Catalog of Infrared Spectrograms" on which these correlations are principally based[2] are of a much simpler structure than the steroids considered here. It may therefore be relevant to note that in elaidic acid (III), a band occurs at 968 cm.$^{-1}$ which has been attributed to the *trans*-disubstituted olefin group.[3,4] The spectrum of a liquid film of oleic acid (IV) does not exhibit any pronounced band near 968 nor in the 700–680 cm.$^{-1}$ region, but when such a film is cooled with liquid nitrogen the whole spectrum sharpens to a remarkable degree and a strong band appears at 705 cm.$^{-1}$.

A fuller discussion of the spectra of the compounds mentioned in this paper will be published later; the spectra of calciferol and vitamin D_3 have been published elsewhere.[5]



III



IV

Experimental.—The steroid spectra were determined in carbon disulfide solution using a Perkin-Elmer Model 12C spectrometer.

NOTE ADDED IN PROOF.—Subsequent to the acceptance of this mss. for publication, a similar observation has been reported by Turnbull, Whiffen and Wilson (*Chem. and Ind.*, **33**, 626 (1950)).

Acknowledgments.—The author is indebted for the gift of compounds to Sir Ian Heilbron and Dr. D. H. R. Barton of Imperial College, London; Dr. M. L. Tainter of Winthrop Chemical Co., Rensselaer, N. Y.; and Professor E. R.

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(1) Crowfoot and Dunitz, *Nature*, **162**, 608 (1948).

(2) Barnard, Bateman, Harding, Koch, Sheppard and Sutherland, *J. Chem. Soc.*, 915 (1950).

(3) Rao and Daubert, THIS JOURNAL, **70**, 1102 (1948).

(4) Lemon and Cross, *Can. J. Research*, **27B**, 610 (1949).

(5) Jones, *Chemistry in Canada*, **6**, 26 (94) (1950).