

## Letters to the Editor

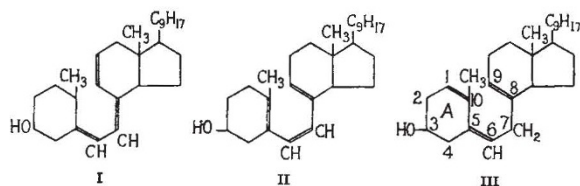
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NOTES ON POINTS IN SOME OF THIS WEEK'S LETTERS APPEAR ON P. 1078.

CORRESPONDENTS ARE INVITED TO ATTACH SIMILAR SUMMARIES TO THEIR COMMUNICATIONS.

## Ring Structure of Calciferol

ALTHOUGH calciferol has been shown to be isomeric with ergosterol ( $C_{28}H_{44}O$ ), comparatively little information has hitherto been adduced concerning the detailed structure of this vitamin. According to Windaus, Linsert, Lüttringhaus and Weidlich<sup>1</sup> (compare also Askew *et alia*<sup>2</sup>) perbenzoic acid titration shows the presence of three ethenoid linkages, from which it follows that calciferol contains a tetracyclic ring structure. In contrast to this observation, Kuhn and Möller<sup>3</sup> have found by hydrogenation that calciferol contains four ethenoid linkages, a result which we have confirmed. Calciferol cannot therefore be a tetracyclic compound. Further evidence in support of this view arises from the work of Lettré<sup>4</sup>, who on dehydrogenation of calciferol failed to obtain Diel's hydrocarbon ( $C_{18}H_{16}$ ). Again, this author has demonstrated that tachysterol, which is a direct intermediate in the photochemical conversion of ergosterol into calciferol, is also tricyclic, probably having the constitution I or II.



During the past year, we have been studying the oxidative degradation of both calciferol and calciferyl acetate, and have found that, with either chromic anhydride or potassium permanganate, an oily aldehyde is obtained, characterised by its well crystalline semicarbazone, m.p.  $242^{\circ}$ . Analysis of the latter shows that the aldehyde has the formula  $C_{21}H_{34}O$ , from which it follows that the disrupted fragment must include the hydroxylated ring A, which consequently cannot be fused to the remainder of the cyclic system as in ergosterol.

Our analytical data for the semicarbazone appear to preclude the formula  $C_{21}H_{32}O$  for the aldehyde, indicating that one of the ethenoid linkages of calciferol is present in ring A. On this evidence, formula III is suggested for the vitamin, the formation of the aldehyde  $C_{21}H_{34}O$  occurring by simple rupture of the  $\Delta^{6,7}$  ethylene linkage. It must be observed that the location of the ethylene linkages at  $\Delta^{1,10}$  and  $\Delta^{8,9}$  is provisional and remains to be confirmed.

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<sup>1</sup> *Ann.*, **492**, 226; 1932.

<sup>2</sup> *Proc. Roy. Soc.*, B, **103**, 340; 1931.

<sup>3</sup> *Z. angew. Chem.*, **47**, 145; 1934.

<sup>4</sup> *Ann.*, **511**, 280; 1934.

## Colorimetric Estimation of Œstrin in the Urine of Non-Pregnant Women

LAST year we reported the details of a method by which it is possible to determine the cestrone and cestriol content of human pregnancy urine colorimetrically with a reasonable degree of accuracy<sup>1</sup>. Since the publication of our paper we have received numerous inquiries as to whether the method can be used for the determination of the œstrin content of urine of non-pregnant women. As this question seems to be one of some general interest, and since in our paper we made no mention of the possibility of using our method for this purpose, we wish to take this opportunity of mentioning briefly our views on the matter.

We have made numerous attempts to estimate the cestrone and cestriol in the urine of non-pregnant women by our colorimetric method, but so far the results have been far from encouraging. Owing to the relatively small amounts of œstrin present it is necessary to carry out the colour reaction in a much larger quantity of extract than we use in the case of pregnancy urines, and hence the colour reaction is carried out in fractions which contain a relatively much higher proportion of non-œstrogenic phenolic substances. The final colour obtained in such tests is a dirty brown instead of a clear pink as is obtained with pregnancy urine extracts. This colour can, of course, be analysed with the Lovibond tintometer, but we do not feel at all confident that the red component of the brown colour can be accepted as a true measure of the œstrin present.

We feel, therefore, that our method as described for pregnancy urine is of little value for the estimation of the much smaller amounts of œstrin present in the urine of non-pregnant women, and we cannot advise its use for this purpose.

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<sup>1</sup> *Biochem. J.*, **23**, 1603; 1934.

## Radio-Transmission of Cosmic Ray Data from the Stratosphere

ON April 1, 1935, an apparatus recording cosmic rays by the coincidence method and transmitting the signals by Moltehanoff's radio method, ascended to the stratosphere from the Institute of Aerology at Slostsk (25 km. from Leningrad). The construction of the apparatus and observations with it obtained in an aeroplane flight have already been described<sup>1</sup>.

The coincidences were recorded by a relay, which switched on the anode circuit of the radio-oscillator. The radio-signals made in this way were received and counted at the earth's surface by three observers.

Besides the coincidences, the apparatus transmitted at more or less regular intervals the total