LETTER

OXIDATION OF CORTISOL BY BiO\textsuperscript{-3}

To the Editors:

Recently Appleby et al. (1955) have reported a skilful method for indirect analysis of 17-hydroxycorticosteroids in sensu lato. The technique is based on the principle by which 17-hydroxycorticosteroids are able to be converted into 17-ketosteroids by the oxidation with bismuthate in 50\% acetic acid.

In a reinvestigation of the method, I noted that the yields of 17-ketosteroid form the C-21, 17-diol-20-one type steroids in this procedure are only about half of the original steroid, though the C-21, 20, 17-triol type steroids are oxidized completely into 17-ketosteroid. No original steroids, however, were found in both series of experiments. So this suggested a strong possibility that a part of cortisol would be converted into the another steroid giving no Zimmermann's reaction. The fact that considerable amounts of steroid have been found exhibiting the ferricyan reducing reaction in oxidized product gave support to this possibility.

In order to gain more knowledge of the properties of any unidentified steroid, the oxidized product of cortisol was chromatographed on the alumina column. Since all of them were eluted off in the 0.3\% methanol-benzene fraction, the work was in vain. Aiming at better separation a paper chromatography was attempted. Just as expected, on the paper chromatogram using ligroin-propylene glycol system (Savard, 1953) it was proved there were two steroids. As shown in the contact photogram by the ultraviolet scanning (Fig. 1), the new separated steroid migrated more slowly than the known steroid, \( \Delta^4 \)-androstene-11-ol-3, 17-dione.

Various tests were tried to identify the new steroid. The steroid crystallized in needle shape and melted at 188\(^\circ\)C (uncor.). It was measurable quantitatively by the color produced by the ferricyan reducing reaction (Aizawa, 1954), suggesting the presence of ketone group at C-20. And none of the reactions, such as the formaldehydo-, acetaldehydogenic reactions, the TTC-reducing reaction, and the ferric chloride (in sulfuric acid and acetic acid) reaction which characterizes testosterone, its ester (Hosoi, 1955) and 17-hydroxycarboxylic steroid, were given.

From this data it would seem that the new steroid is \( \Delta^4 \)-androstene-3-one-11-ol-17-hydroxyaldehyde. Moreover, as an evidence of the lack of C at C-21 the steroid showed a polarity similar to 17-

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ketosteroid; C-21 steroids do not elute off through the column chromatography mentioned above.

It is well established that a part of cortisol in circulation is oxidized to 11-oxigenated 17-ketosteroids. But so far as I know, no experiments on its oxidation processes have yet been made. Would this produce the tentative 17-hydroxyaldehyde steroid or the 17-hydroxycarboxylic steroid as an intermediate metabolite to 17-ketosteroids? If so, those steroids should be found in human urine, or their administration should cause the increase of the urinary 17-ketosteroids levels.

I am, however, unable to answer these questions at present, because no expected results were obtained.

Before closing this letter, I wish to express my indebtedness to the late Professor Mutsuo Heki for his invaluable advice and encouragement.

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REFERENCES