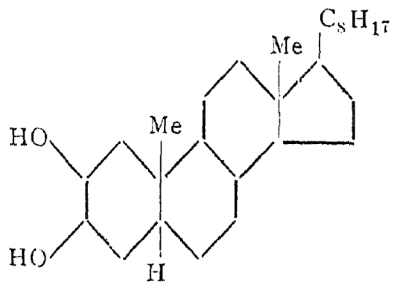
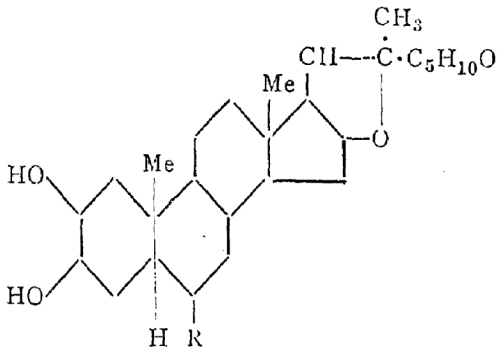
The Configurations of the C_2 and C_3 Hydroxyl Groups in Gitogenin and Digitogenin

IT has been previously mentioned[1] in connection with the 2:3-dihydroxycholestanes (I) that the presence of the hydroxyl group at C_2 may not interfere with the digitonin precipitability and that of the four isomers of 2:3-dihydroxycholestanes, two, in which the C_3 hydroxyl groups are of the normal (β-) configuration, should precipitate with digitonin. This is now indirectly confirmed by the recent reports of Noller[2] and of Marker and Rohrman[3] that the 2:3-dihydroxysteroid sapogenins, gitogenin (II, R = H) and digitogenin (II, R = OH) precipitate with digitonin, contrary to what had been previously reported by Tschesche and Hagedorn.[4]

There are four theoretical possibilities of the relative configurations of the C_2 and C_3 hydroxyl groups in these sapogenins corresponding to the four stereoisomeric forms of 2:3-dihydroxycholestane[1] (of which in one the hydroxyl groups are in the *trans* and in the rest



(I)



(II)

in the *cis* positions). Basing on the report of Tschesche and Hagedorn[4] and also the behaviour of the three isomeric 2:3-dihydroxy*trans* decalins,[5] it was suggested[6] that the C_2 and C_3 hydroxyl groups in gitogenin and digitogenin are in transpositions to each other, the C_3 hydroxyl groups being of the *epi* (α-) configuration. Due to the observations of the American authors mentioned above, this suggestion is now revised.

Assuming the precipitation with digitonin to be having the same significance for the steroid sapogenins as for the sterols (Noller[2]), it is to be concluded that C_3 hydroxy group in gitogenin and digitonin is of the β-configuration—*i.e.*, it is *cis* to the C_{10} methyl group. By the other hydroxyl group at C_2, occupying the two possible positions *cis* or *trans* with reference to the C_{10} methyl group, two forms are possible in which the two hydroxyl groups (which are *cis* to each other in both forms) are unsymmetrical or symmetrical respectively about the plane of the carbon atoms 2, 3, 5 and 9. (These two forms correspond to those of B and A respectively of 2:3-dihydroxy*trans*decalin[5].) By

analogy with the behaviour of the 2:3-dihydroxy*trans*decalin of form B, we should expect the sapogenins to isomerise to the *trans* form on treatment with acid if these hydroxyl groups possessed the unsymmetrical configuration. Since this has not been observed, it may be concluded that in gitogenin and also in digitogenin the hydroxyl groups at C_3 and C_2 (which are in *cis* positions to each other) are *cis* and *trans* respectively with respect to the C_{10} methyl group.

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[1] Ganapathi, *Curr. Sci.*, 1939, **8**, 360.
[2] Noller, *J. Amer. Chem. Soc.*, 1939, **61**, 2717.
[3] Marker and Rohrman, *Ibid.*, 1939, **61**, 2724.
[4] *Ber.*, 1935, **68**, 2248.
[5] Ganapathi, *Ber.*, 1939, **72**, 1381.
[6] Ref. 1 footnote.