LETTERS TO THE EDITOR

Interaction of Atomic Energy Levels Part II

In continuation of the work previously reported in *Current Science*,[1] the spectra of mercury and of cadmium and of their mixture have been studied by the same method as before. Some lines of the two elements have disappeared in the spectrum of the mixture, while some lines not to be seen in the spectra of the individual metals make their appearance. Other lines suffer a greater or less modification of intensity, but many lines remain unaffected. The following list contains all the lines thus modified. Brackets indicate that the change of intensity is not large.

Cadmium Lines

Weakened

[6438·47 ($5^1P_1 - 5^1D_2$)]
6329·91 ($5^1P_1 - 5^3D_1$) (absent)
6325·19 ($5^1P_1 - 5^3D_2$)
6111·52 ($6^3S_1 - 8^3P_1$) (absent)
6099·18 ($6^3S_1 - 8^3P_2$) (absent)
2881·23 ($5^3P_1 - 6^3D_1$)
2880·77 ($5^3P_1 - 6^3D_2$)
2868·26 ($5^3P_2 - 8^3S_1$)
2836·90 ($5^3P_0 - 6^3D_1$)
2775·00 ($5^3P_1 - 8^3S_1$)
2733·88 ($5^3P_0 - 8^3S_1$)

Strengthened

2677·64 ($5^3P_1 - 7^3D_2$) (new)
2660·40 ($5^3P_2 - 8^3D_3$) (new)
2602·18 ($5^3P_2 - 9^3D_3$) (new)
2288·02 ($5^1S_0 - 5^1P_1$)
2265·05 (Cd II $5s\,^2S_{1/2} - 5p\,^2P_{1/2}$) (new)

Mercury Lines

Weakened

5790·66 ($6^1P_1 - 6^1D_2$)
5789·69 ($6^1P_1 - 6^3D_1$)
5769·60 ($6^1P_1 - 6^3D_2$)
[5460·74 ($6^3P_2 - 7^3S_1$)]
3983·92 (Hg II $5d^96s^2\,^2D_{5/2} - 5d^{10}6p\,^2P_{3/2}$) (absent)
{ [3663·28 ($6^3P_2 - 6^1D_2$)]
{ [3662·88 ($6^3P_2 - 6^3D_1$)]
[3654·83 ($6^3P_2 - 6^3D_2$)]
[3650·15 ($6^3P_2 - 6^3D_3$)]
2804·46 ($6^3P_2 - 8^3D_2$)
2803·48 ($6^3P_2 - 8^3D_3$)
2698·85 ($6^3P_2 - 9^3D_3$) (absent)
2639·93 ($6^3P_2 - 10^3D_3$) (absent)
2603·15 ($6^3P_2 - 11^3D_3$) (absent)
2578·44 ($6^3P_2 - 12^3D_3$) (absent)

Strengthened

[4077·83 ($6^3P_1 - 7^1S_0$)]
2655·13 ($6^3P_1 - 7^1D_2$)
2653·68 ($6^3P_1 - 7^3D_1$)
2652·04 ($6^3P_1 - 7^3D_2$)
[2536·52 ($6^1S_0 - 6^3P_1$)]
2534·80 ($6^3P_0 - 7^3D_1$)
2464·02 ($6^3P_2 - 9^3S_1$) (new)

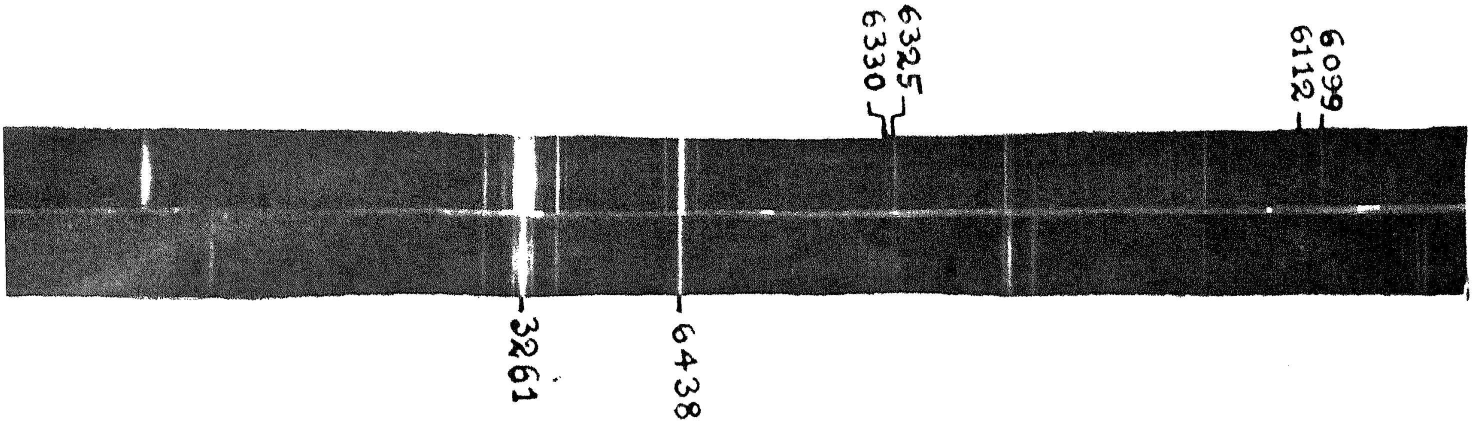


FIG. 1

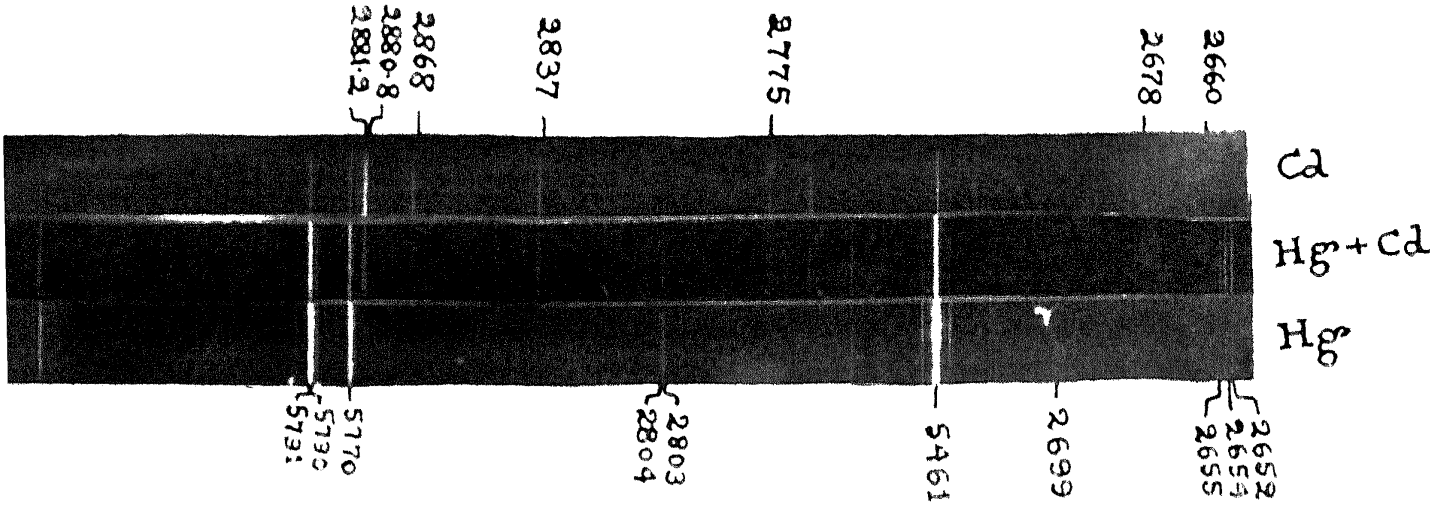


FIG. 2

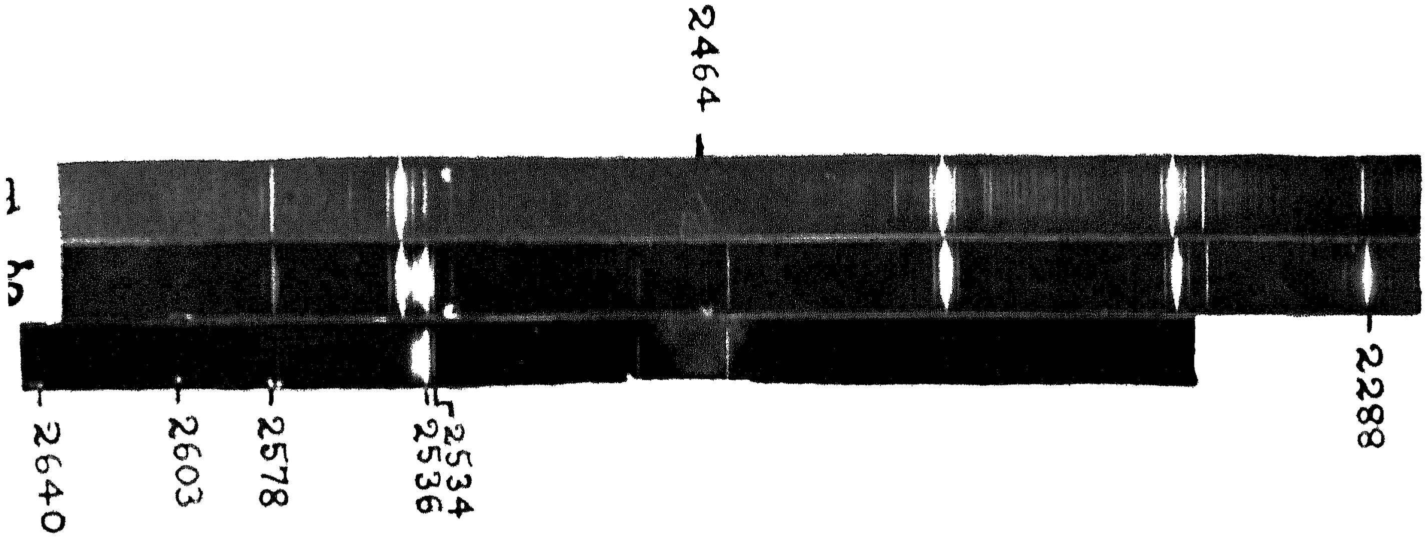
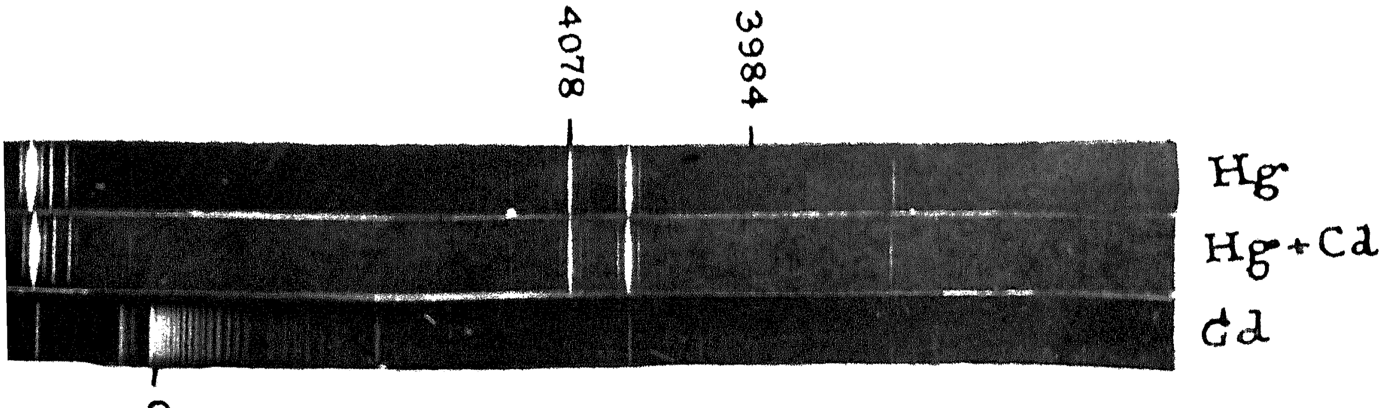


FIG. 3



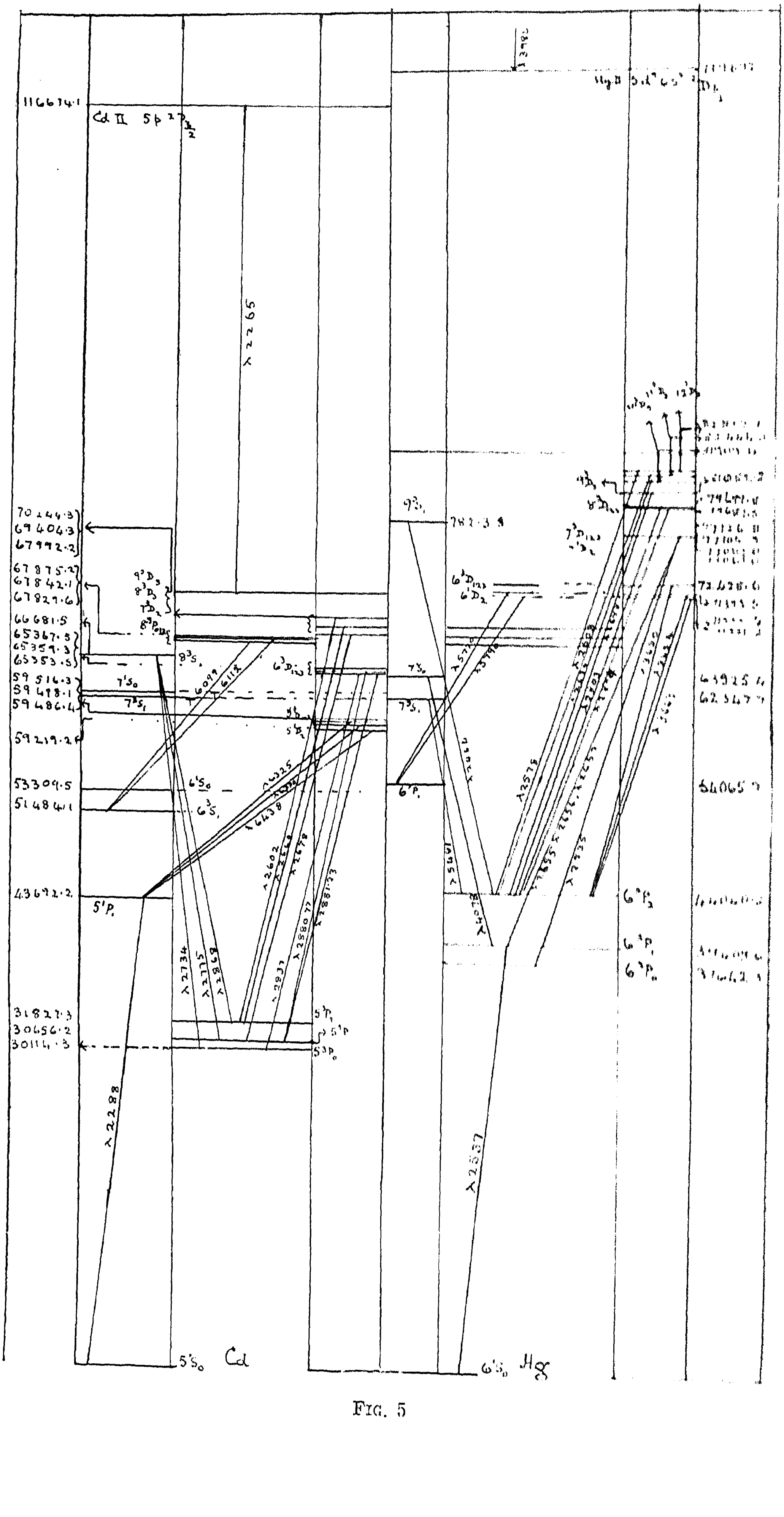

116614·1
Cd II 5p ²P3/2
λ2265
70144·3
69404·3
67992·2
67875·2
67842·1
67829·6
66681·5
65367·5
65359·3
65353·5
59516·3
59498·1
59486·4
59219·2
53309·5
51484·1
43692·2
5¹P₁
31827·3
30656·2
30114·3
λ2288
5¹S₀ Cd
λ2537
6¹P₁
6¹S₀ Hg

FIG. 5

The resonance line 2537 of mercury shows complete self-reversal in mercury but no trace of reversal in the mixture. The 2540 band accompanying 2537 is present in mercury and in the mixture with cadmium, whereas it disappeared in the mixture with zinc. Similarly the ZnH bands appearing in zinc continued strong in the mixture with mercury, but the CdH bands, though present in cadmium, disappeared in the mixture of mercury and cadmium. The resonance line of zinc 3076 was weaker than 3345 in pure zinc but became stronger than the latter in the presence of mercury; on the other hand, the cadmium resonance line 3261 was stronger than 3610 in cadmium and continued to be so in the mixture.

Of the various instances of alteration of line intensity enumerated above, the strengthening of 2288 is the easiest to explain. The excitation energy of 5^1P_1 of Cd is 43692·2 cm,$^{-1}$ while the metastable 6^3P_2 state of mercury has an energy very close to this, *viz.*, 44040·2 cm.$^{-1}$. Hence the probability of the latter exciting the former is high and so 2288 is strengthened. The slight weakening of 5461 shows that some atoms are removed from the 7^3S_1 state without dropping to the 6^3P_2-level. Taking this with the fact that the Cd lines 6438 ($\nu = 15527$ cm.$^{-1}$), 6330 ($\nu = 15794$ cm.$^{-1}$) and 6325 ($\nu = 15805$ cm.$^{-1}$) are weakened, we may assume that the energy of these lines raises the Hg atom from the 7^3S_1 state to the 7^3D_2, 7^3D_1 and 7^1D_2 states which differ from 7^3S_1 by 14757·6, 14734·3 and 14713·3 cm.$^{-1}$ respectively, say, by impacts of the second kind. This will then explain the brightening of 2655, 2654, 2652 and 2534. All these lines, except 2534, involve transitions to the 6^3P_1 state, so that the population of this state is increased. Hence we should expect 2537 to be brightened, as is actually the case. The brightening of 2655, 2654, 2652 and 2534 can also be due to mercury atoms in the 6^3P_2 state (energy 44040·2 cm.$^{-1}$) being raised to the 7^3D_2, 7^3D_1 and 7^1D_2 states by interaction with the metastable 5^3P_2 state of Cd (energy 31827·3 cm.$^{-1}$). The energies of 7^3D_2, 7^3D_1 and 7^1D_2 are 77061·0, 77082·0 and 77105·3 cm.$^{-1}$ respectively, and, the sum of the energies of 6^3P_2 of Hg and 5^3P_2 of Cd being 75867·5 cm.$^{-1}$, the deficiency is within what can be supplied by thermal energy. In a similar way, the energy of 6112 ($\nu = 16358$ cm.$^{-1}$) and 6099 ($\nu = 16391$) of Cd which are weakened must have been used to raise the Hg atom in the 7^3S_1 state to the 9^3S_1 state, the difference between which is 15866·1 cm.$^{-1}$. The new appearance of 2664 is thus explained. Of the cadmium lines which are weakened, the upper state of 2881·2 and 2836·9 is 6^3D_1 of energy 65353·5 cm.$^{-1}$, that of 2880·8 is 6^3D_2 (energy 65359·3 cm^{-1}) and that of 2868·3, 2775·0 and 2733·9 is 8^3S_1 (energy 66681·5 cm.$^{-1}$). These energies are sufficiently near the excitation energy of 7^1S_0 of Hg which is 63925·4, to make it probable that the strengthening of 4078 is due to this interaction. 5791, 5790, 5770, 3663, 3654 and 3650, all of which are weakened, have $6^3D_{1,2,3}$ and 6^1D_2 as their upper levels. Their excitation energies are 71333·4, 71393·5, 71428·6 and 71330·2 cm.$^{-1}$ and these are sufficiently near 7^3D_2, 8^3D_3 and 9^3D_3 of Cd (energies 67992·5, 69404·3 and 70250 cm.$^{-1}$) to explain the new appearance of 2678, 2660 and 2602 of Cd.

The weakening of 2804, 2803, 2699, 2640, 2603, and 2578 means the depopulation of 8^3D_2, 8^3D_3, 9^3D_3, 10^3D_3, 11^3D_3 and 12^3D_3 of Hg. The excitation energies are 79687·5, 79699·8, 81082·2, 81909·0, 82444·0 and 82812·1 cm.$^{-1}$. If these energies are added to the energy of the metastable $^3P_2$ state of Cd (= 31827·3 cm.$^{-1}$) we come sufficiently near to the excitation energy of 2265 of Cd II (116674·1 cm.$^{-1}$) for the difference to be capable of being supplied by thermal energy. The excitation energy of 3984 of Hg II (119692 cm.$^{-1}$) which has disappeared is also capable of explaining the new appearance of 2265. Since the excitation energies of 8^3D_2 . . . 12^3D_3 of Hg are higher than the ionization energy of Cd, the explanation of the weakening of 2804, etc., must proceed in some such way as the above, but too much weight should not be attached to the disappearance of such weak lines as these.

Apart from explaining the observed changes of intensity, some clarification is required for the fact that no interaction has been found between other levels of Hg and Cd which are quite close to each other, *e.g.*, 6^1P_1 of Hg and 6^1S_0 of Cd, 7^3S_1 and 7^1S_0 of Hg and 7^3S_1 and 7^1S_0 of Cd, x^3P of Hg and 8^3P and 8^1P of Cd and so on. The theory of the interaction of atomic energy levels must be better developed for this to be possible. The present work is intended to provide an experimental basis for such a development. The transitions for the various wave-lengths are indicated in the level diagram appended (Fig. 5).

In conclusion it is a pleasure to record our thanks to Prof. A. Venkat Rao Telang, M.A., F.Inst.P., for his encouragement and many facilities afforded to us.

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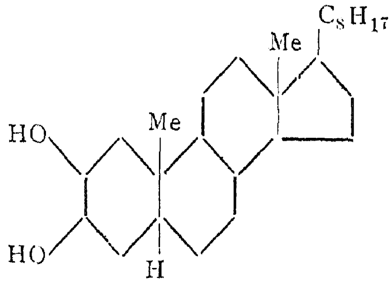
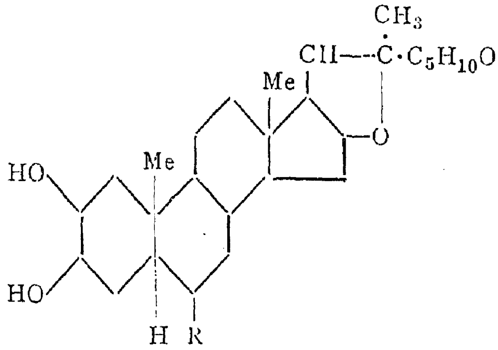
The Configurations of the C_2 and C_3 Hydroxyl Groups in Gitogenin and Digitogenin

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