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ステロイドホルモンからのフリーラジカル生成と構造活性相関*

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Steroid hormones including glucocorticoids, progestins, androgens and estrogens show distinct ESR spectra in alkaline dimethyl sulfoxide (DMSO). An ESR spectrum of cortisol showed the simplest structure consisting of a double and a small singlet, while that of corticosterone further split into five peaks. Both compounds, however, exhibited identical spectrum of triplets in alkaline DMSO-d_6. Hydrogenation at position 17 as wells as 20 increased the complexity of the spectrum. These results could be best explained by assuming the oxy radical at position 20. On the other hand, progestins shared the same ESR spectra with such androgens as testosterone. The hyperfine structures were not altered by chemical modifications at positions, 17, 16 and 11 in this series of derivatives. Androgens with saturated A rings gave completely different spectra. These results suggest that active sites of free radicals were located close to A and B rings and the most likely at position 3. Estrogen series further strengthened the latter possibility, since phenoxy radicals could be expected in this case from extrapolation of an estrogens analog, diethylstilbestrol. Esterification at position 3 of estrogens did not block the radical formation in alkali but glucuronization at position 3 completely abolished the production of free radicals.

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