SYNTHESIS OF 3β-ACETOXYANDROST-5-ENO[17,16-c](5-CYANO-2-METHYLPYRIDINE-6(1H)-THIONE) AND THE CORRESPONDING SELENONE AND THEIR ALKYLATION WITH CHLOROACETONITRILE

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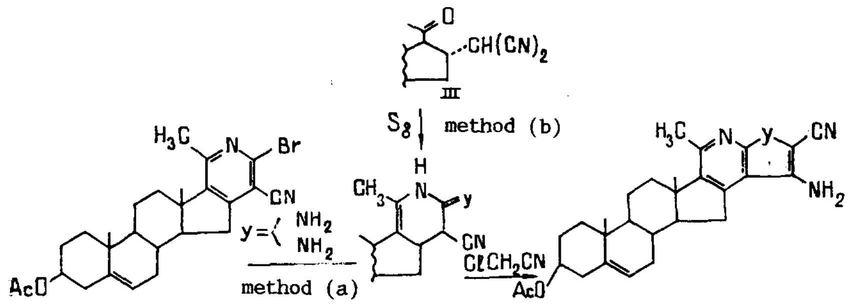
Substituted 3-cyanopyridine-2(1H)-thiones and -selenones are obtained by the reaction of 2-halogenopyridines with thiourea [1] and selenourea [2]. When 3β-acetoxyandrost-5-eno[17,16-c](2-bromo-3-cyano-6-methylpyridine) was heated with thio- or selenourea in ethanol in the presence of alkalies, followed by acidification of the mixture with dilute hydrochloric acid, we obtained 3β-acetoxyandrost-5-eno[17,16-c](5-cyano-2-methylpyridine-6(1H)-thione) (IIa) or the corresponding selenone (IIb).



I IIa,b IVa,b

II,IV,V = S (a); Se (b)

The thione (IIa) was also obtained by the treatment of the acetate of 16α-dicyanomethyl-3β-hydroxypregn-5-en-20-one (III) with powdered sulfur in boiling ethanol in the presence of morpholine. It was impossible to synthesize the corresponding selenone by this method.

Alkylation of the thione (IIa) and the selenone (IIb) with chloroacetonitrile in an inert atmosphere at room temperature in dimethylformamide under the action of KOH led to the formation of 3β-acetoxy-androst-5-eno[16,17-c](3-amino-2-cyanothieno)[3,2-e](2-methylpyridine) (IVa) and the corresponding selenopyridine (IVb).

Compound (IIa): Y=S; the yield by method *a* amounted to 46% and by method b to 84%; mp 277-279° (decomp.). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ (nm): 236, 311, 391 (log ε 3.97, 4.28, 3.51). IR spectrum: ν_{max}^{KBr} (cm^{-1}): 1731 (O–C=O), 2230 (C≡N). ^1H NMR spectrum (DMSO-d_6; δ, ppm): NH (13.40 br.s, 1 H), =CH (5.39, m, 1 H), O–C^{3}H (4.47 m, 1 H), 18-H_3 (0.93, s, 3 H), 19-H_3 (1.04, s, 3 H), CH_3CO (1.99, s, 3 H), 6-H_3 (2.29, s, 3 H).

Compound (IIb): Y=Se; yield 43%; mp >300°C (decomp.). IR spectrum, ν_{max}^{KBr} (cm^{-1}): 1734 (O–C=O), 2291 (C≡N).

Compound (IVa): yield 69%, mp 297-298°C (decomp.). IR spectrum, ν_{max}^{KBr} (cm^{-1}): 3250, 3330, 3420, 1630 (NH_2); 2199 (C≡N); 1725 (O–C=O). ^1H NMR spectrum (DMSO-d_6, δ, ppm): NH_2 (6.58, br.s, 2 H), =CH (5.42 m, 1 H), O–CH (4.41, m, 1 H), 18-H_3 (0.94, s, 3 H), 19-H_3 (1.05, s, 3 H), CH_3CO (2.00, s, 3 H), 6-H_3 (2.50, s, 3 H).

Compound IVb: yield 60%, mp 185-187°C (decomp.). IR spectrum ν_{max}^{KBr} (cm^{-1}): 3240, 3310, 3410, 1625 (NH_2); 2192 (C≡N), 1731 (O–C=O). ^1H NMR spectrum (DMSO-d_6, δ, ppm): NH_2 (6.42, br.s., 2 H), =CH (5.39, m, 1 H), O–CH (4.44, m, 1 H), 18-H_3 (0.93, s, 3 H), 19-H_3 (1.04, s, 3 H), CH_3CO (1.99, s, 3 H), 6-H_3 (2.50, s, 3 H).

The results of the elementary analysis of all the compounds agreed with the calculated figures.

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ENZYMATIC OXIDATION OF LIGNIN AND OF COMPOUNDS MODELING IT.

IV. CHARACTERISTICS OF THE CHEMILUMINESCENCE ON PEROXIDASE OXIDATION OF α-GUAIACYLPROPANONE

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We have previously established that the peroxidase oxidation of lignin and of a number of its phenylpropane structures, including α-guaiacylpropanone, takes place through a stage of the formation of excited intermediates the deactivation of which leads to an emission of radiation in the visible region of the spectrum – chemiluminescence (CL) [1, 2]. The emission spectra of the excited chromophores of lignin [3] and of a number of its structural units are practically identical (Fig. 1), which points to a similarity of the mechanisms of the deactivation of the excited intermediates. The appearance of radiation in the red region of the spectrum (λ_{max} 630 nm) is explained by the formation of singlet oxygen in the system. Emission in the 560-nm region is connected with the radiative deactivation of a carbonyl group in the excited triplet state. It is still not clear whether it is the carbonyl group of the substrate present in the α-position that is excited or whether, in the process of peroxidase oxidation, quinones (of the p-quinone type) are formed, the excited carbonyl groups of which also radiate in the 560-nm region on deactivation [4].

In spite of the identity of the emission spectra, the deactivation of the excited chromophores formed on the peroxidase oxidation of α-guaiacylpropanone has a number of characteristic features which appear in an analysis of the kinetic curves of the quenching of the CL. The kinetic curve of CL on the peroxidase oxidation of lignin is characterized by a sharp flash of light followed by an exponential dying away of the radiation [1]. In contrast to the peroxidase oxidation of lignin, the kinetic curve of the CL on the oxidation of α-guaiacylpropanone has two maxima of the intensity of emission. In the first stage of the process, during a time of less than 20 sec, the intensity of emission rises rapidly from 0 to I_{init} (Fig. 2). The time to reach the first maximum and its intensity are determined by the concentration of peroxidase. In the second stage of the process, after some fall in emission, there is a slower rise in intensity to a maximum (I_{max}) and a subsequent dying away of the radiation.

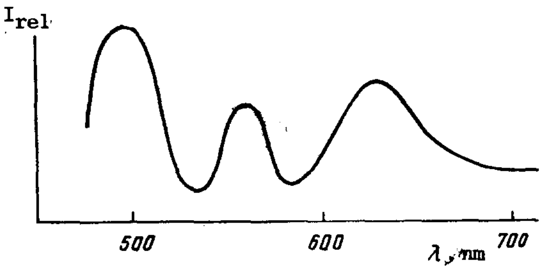

Fig. 1. Radiative deactivation spectrum of excited intermediates from α-guaiacylpropanone.

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