

## THE HYDROGENATION OF CYTISINE OVER NICKEL IN ETHANOL

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In the hydrogenation of cytisine [1] over Raney nickel in ethanol, two products are formed one of which is identical with tetrahydrocytisine [2], while the second, with the composition  $C_{13}H_{22}N_2O$ , has, after two recrystallizations from petroleum ether, mp 62-63° C,  $[\alpha]_D^{20} -88.67^\circ$  (c 2.03, ethanol),  $R_f$  0.79 (in a thin layer of  $Al_2O_3$  in the acetone system).

The second product differs in composition from tetrahydrocytisine by a  $C_2H_5$  group. Its NMR spectrum lacks the signals of the pseudoaromatic protons of a pyridine ring. The general shape of the spectrum is characteristic for hydrogenated derivatives of cytisine with a substituent at the N-H bond. The triplet of this substance at 0.97 ppm corresponds in its chemical shift to a C-methyl group; the splitting of the signal into a triplet shows the presence of a neighboring  $CH_2$  group whose signal is located in the 1.8-2.5-ppm region and masks the signals of the cytisine skeleton. Thus, we may assume with confidence that in the second product an ethyl group is present as substituent. To confirm its structure, by ethylating tetrahydrocytisine with ethyl bromide we obtained N-ethyltetrahydrocytisine with mp 63-64° C. In a direct comparison, the two substances proved to be identical.

The results obtained show that during the hydrogenation of cytisine in ethanol partial replacement of the hydrogen of the secondary nitrogen by an ethyl group takes place with the formation of N-ethyltetrahydrocytisine.

When cytisine is hydrogenated in methanol, in addition to tetrahydrocytisine, a product is formed which is identical with the methyltetrahydrocytisine that we obtained (for comparison) by the hydrogenation of methylcytisine.

## REFERENCES

1. M. Spath and F. Galinovsky, Ber., **65**, 1526, 1932; **66**, 1338, 1933.
2. M. Freund and P. Norkheimer, Ber., **39**, 814, 1906.

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