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A STUDY OF THE PRODUCTS OF THE DEHYDROGENATION OF LAGOCHILIN

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We have studied the products of the dehydrogenation of lagochilin over Raney nickel [1]. Together with the desired product, a series of by-products was formed the number of which depended on the method of activation, the size of the catalyst particles, the ratio of the amounts (by weight) of the latter and of the initial lagochilin, and the depth of dehydrogenation. Depending on the above-mentioned factors, the number of by-products ranged from 4 to 7.

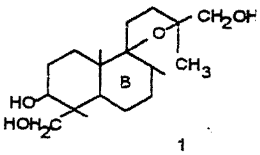
The mother solution after the isolation of lagochilin and separation on a column gave anhydrolagochilin [2] and substance (1) with mp 124-126°C (from isopropanol). The latter proved to be the main by-product (with a yield of 35-40% on the lagochilin) from the dehydrogenation of lagochilin. It dissolved in chloroform, alcohol, and pyridine but not in water, and remained unchanged in alkaline and acid solutions.

In the weak-field region of the PMR spectrum of substance (1) (100 MHz, $CDCl_3$, ppm, J, Hz) a doublet of doublets was observed at 3.64 ppm, a two-proton four-component signal at 3.55 ppm, and two doublets with the same SSCC, J = 10.7 Hz, at 3.40 and 3.26 ppm. It was shown by the double-resonance method that the four-component signal at 3.55 ppm was a superposition of two doublets, at 3.53 and 3.56 ppm, these being components of two *AB*-systems and having partners at 3.26 and 3.40 ppm, respectively. By analogy with the spectrum of lagochilin and its derivatives [3, 4], it may be assumed that the chemical shifts and the nature of the splitting of the signals in the weak-field region corresponded to the signals of H-3 and nonequivalent signals of the protons of methylene groups at C-16 and C-18. The characteristic triplet of methylene protons at C-15 usually observed in the spectra of lagochilin derivatives in this weak-field region was absent.

The addition of a few drops of trifluoroacetic acid (to reveal the signals of hydroxy groups) led to the acetylation of the hydroxy groups, identified by the appearance of additional signals. After the end of the reaction (~2 days), as a result of the addition of trifluoroacetyl groups all the signals considered above had uniformly shifted downfield [4, 5]. Consequently it may be concluded that there were hydroxy groups at C-3, C-16, and C-18, as in lagochilin.

In the strong-field region of the spectrum of (1) there was a "methylene hump" and the signals of the three methyl groups at C-4, C-8, and C-10 that are characteristic for lagochilin. In addition to these, the spectrum of (1) contained an isolated peak of another methyl group at 1.34 ppm. Analysis of the ^{13}C NMR spectra (25 MHz, Py) of lagochilin and substance (1) [6] showd that in the spectrum of (1) there were the signals of two fewer methylene groups and of one more methyl group.

The mass spectrum of (1) showed the peak of the molecular ion with *m/z* 326 and three characteristic peaks of ions with *m/z* 169, 181, and 194, formed by the cleavage of ring *B* in the molecule under investigation. On the basis of its PMR, ^{13}C NMR, and mass spectra, and its elementary analysis the following structure has been proposed for (1):



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It is known that lagochilin has four alcohol groups, and the low yield of the desired product is due to the fact that on dehydrogenation all the hydroxy groups undergo change. The results of a study of the by-products and their yields have shown

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that the dehydrogenation of lagochilin by Raney nickel takes place in several directions. The C-15 alcohol group undergoes a deep change, apparently being split off from the molecule of the initial substance in the form of formaldehyde. The C-14 methylene group is then converted into a methyl group through the migration of a hydrogen atom from the C-15 alcohol group.

The formation of (**1**) is explained by the fact that dehydrogenation was carried out in an anhydrous medium at a high temperature.

Thus, on the basis of elementary analysis and spectral characteristics we propose for the main by-product of the dehydrogenation of lagochilin by Raney nickel the structure of 3,16,18-trihydroxy-9,13-epoxy-15-norlabdane.

REFERENCES

1. U. N. Zainutdinov, Kh. Khaitboev, M. A. Safaev, R. Islamov, and Kh. A. Aslanov, Khim. Prir. Soedin., 38 (1994).
2. M. M. Abramov, Dokl. Akad. Nauk UzSSR, No. 3, 41 (1958).
3. O. S. Chizhov, A. V. Kessenikh, I. P. Yakovlev, B. M. Zolotarev, and V. A. Petukhov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 1983 (1970).
4. Z. I. Mavlyankulova, U. N. Zainutdinov, F. G. Kamaev, and Kh. A. Aslanov, Khim. Prir. Soedin., 82 (1978).
5. N. S. Bhacca and D. H. Williams, Applications of NMR Spectroscopy in Organic Chemistry, Holden-Day, San Francisco (1964).
6. O. C. Chizhov, Yu. S. Ryabokobylko, and A. V. Kessenikh, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1603 (1979).