THE STRUCTURE OF GRANDICIN AND GRANDULIN

L. P. Nikonova and G. K. Nikonov

UDC 547.913:547.2

Continuing a study of grandicin (I) and grandulin (II), isolated previously from Inula grandis Schrenk [1], and of their derivatives by NMR spectroscopy (JEOL-60 instrument, $CDCl_3$), we have now established their structure.

The spectrum of (I) has doublets at 5.96 and 5.40 ppm, J = 2.7 Hz (protons of an exocyclic methylene group on a lactone ring), multiplets at 4.64 and 3.05 ppm (1H each, lactone proton and proton vicinal to it), two singlets at 2.03 and 1.00 ppm (3H each, protons of methyl groups on a double bond and a tertiary carbon atom, respectively). The multiplicity of the signal of the lactone proton and its half-width (28 Hz) show that the lactone ring is in the linear position and has a trans linkage. A signal at 2.07 ppm corresponds to the protons of a methyl group adjacent to a carbonyl keto group located in a side chain (2,4-dinitrophenylhydrazone with mp 189-190°C).

The catalytic hydrogenation of (I) formed only a dihydro derivative (mp 47°C, M^+ 260), in the NMR spectrum of which the signals of the vicinal protons had disappeared and the IR spectrum of which contained bands at 1660 and 823 cm^{-1}, showing the presence of one double bond in its molecule. The NMR characteristics exclude the possibility that (I) is a germacranolide or a guaianolide. The deuteration of (I) gave a product with M^+ 253, which shows the presence of five hydrogen atoms undergoing deuterium exchange in the α position to the carbonyl group. In its NMR spectrum the singlet at 2.03 had disappeared, and the total integral intensity of the protons had decreased by five units (CH_3COCH_2-grouping). A two-proton multiplet at 0.42 ppm corresponds to protons present in a three-membered ring [2]. With the composition $C_{15}H_{20}O_3$, and the presence of one C = C bond, substance (I) must have a tricyclic structure [lactone, three-membered and six- or seven-membered ring, and an open chain with the CH_3COCH_2-group]; i.e., it corresponds to the lactone carabrone [3], which was confirmed by comparing their physicochemical constants.

In the NMR spectrum of (II), there are broadened singlets at 6.03, 5.52, and 4.71, 4.46 ppm (exocyclic methylene groups at C_4 and C_{11}), a singlet at 0.76 ppm (angular methyl group at C_{10}), and a multiplet at 4.38-4.56 ppm (lactone proton). The chemical shifts of the signals of the vinyl protons at C_4 are close to those of ivalin, ivasperin [5], telekin [6], asperilin [5], and others lacking a hydroxyl at C_3. The presence of the signal of a methine proton in the geminal position to a hydroxy group (multiplet at 3.5-3.95 ppm) shows that the latter is secondary and is located at C_2 (otherwise, this signal would appear in the form of a triplet or a quartet). On the basis of these facts and its physicochemical constants, (II) must be identical with the lactone ivalin [4, 5]. The identity of (I) with carabrone and of (II) with ivalin was shown by comparing their IR spectra with those of authentic samples. The sample of ivalin was kindly given to us by Dr. W. Herz, and the IR and NMR spectra of carabrone by Dr. H. Minato.

LITERATURE CITED

1. L. P. Nikonova and G. K. Nikonov, Khim. Prirodn. Soedin., 133 (1970).
2. J. Emsley, J. Feeney, and L. Sutcliffe, High Resolution NMR Spectroscopy, Pergamon, Oxford (1965-1966).
3. H. Minato, S. Nosaka, and J. Horibe, J. Chem. Soc., 1964, 5503.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Tashkent Pharmaceutical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 679-680, September-October, 1972. Original article submitted April 11, 1972.

4. W. Herz and G. Hogenauer, J. Org. Chem., 27, No. 3, 905 (1962).
5. W. Herz and N. Viswanathan, J. Org. Chem., 29, No. 5, 1022 (1964).
6. B. Venešova, V. Herout, and F. Šorm., Collection Czech. Chem. Commun., 26, No. 5, 1350 (1960); 27, 2916 (1961).