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SPECTRAL FEATURES OF DENUDATINE ALKALOIDS FROM *Delphinium dictyocarpum* AND *D. corymbosum* AND THEIR DERIVATIVES

B. T. Salimov

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PMR and electron-impact (EI) mass spectral data of the denudatine alkaloids with saturated C(16)–C(17) bonds dictysine (**1**), N-ethyl-de-N-methyldictysine (**2**), dehydrodictysine (**3**), corumdizine (**4**), corumdizinine (**5**), and cordizine (**6**) that were isolated from *Delphinium dictyocarpum* DC. or *D. corymbosum* Rgl. have been reported [1-4]. It seemed interesting to compare these data with those for the alkaloids yesoxine (**7**) and gomandonine (**8**) [5, 6], which differ from **1** by the presence of additional oxygen functional groups on C-1 and C-13 and C(15)-hydroxy-C(16),C(17)-epoxy in ring D instead of an α,β,γ-triol. Thus, signals for C(16)–CH_2 protons shift sharply to weaker field in the PMR spectrum, as expected on going from **7** and **8** to **4** and **5**, in which this group forms a methylenedioxy group. However, the chemical shifts (CS) approach values typical of compounds with an open chain. An analogous picture is observed for the PMR spectra of **7** and **8** compared with those of the acetonides of dictysine (**9**) [2] and N-ethyl-de-N-methyldictysine (**10**) [4]. The difference in the CS values for the signals of the C(16)–CH_2 group decreases sharply in the PMR spectrum of the acetonide of dehydrodictysine (**11**) [2], which has a C(15)=O and C(16),C(17)-acetonide.

Examination of models revealed that one of the protons of this group in **11** can be influenced by the strong anisotropic field of the C(15)=O. As a result of this, the corresponding signal undergoes a diamagnetic shift.

The EI mass spectra of **4**-**6** and **10** [3, 4] showed that they undergo fragmentation similar to that of **1**, **3**, and their derivatives [1, 2]. Peaks for ions with *m*/*z* 270 and 186 in the spectra of **4**, **6**, and **10** are due to the presence in them of an N-ethyl instead of an N-methyl. One peculiarity of the fragmentation of **4** and **5** is the appearance of $[M - 1]^+$, $[M - 47]^+$, and $[M - 59]^+$ ions, which is connected with the presence in them of a C(16),C(17)-methylenedioxy group. A distinguishing feature of the fragmentation of **3** and **6**, which have a C-15 carbonyl, is the generation of $[M - 45]^+$ for the former and $[M - 28]^+$ for the latter [3].

The mass spectral results for **7** and **8** [5, 6] lead to the conclusion that the principal fragmentation pathway for them is apparently due to initial rupture of the C(10)–C(20) bond because the base peaks in their spectra are $[M - 17]^+$ or $[M - 43]^+$, which are formed from the molecular ion by loss of the substituent on C-1 [7]. Fragmentation of macrocentrine (**12**) [8], which differs from **2** by additional hydroxyls on C-2 and C-3, is dominated by a process beginning after initial rupture of the C(7)–C(20) bond because the base peak in the spectrum of this compound is the molecular ion. The intensities of the peaks for $[M - 17]^+$ and $[M - 35]^+$ are about the same as those for analogous ions that appear during fragmentation of dictysine (**1**) [1].

These data lead to the following conclusions. If the base peak is the molecular ion and peaks for $[M - 17]^+$, $[M - 35]^+$, and $[M - 91]^+$ appear in the spectra of denudatine alkaloids with a saturated C(16)–C(17) bond, they contain the sequence CH(OH)–C(OH)–CH_2OH in ring D [1, 2]. If $[M - 28]^+$ or $[M - 45]^+$ is the base peak or $[M - 47]^+$ is the base peak and the $[M - 1]^+$ and $[M - 59]^+$ peaks are strong in the spectra of these compounds, they contain a C(15)-carbonyl or C(16),C(17)-methylenedioxy, respectively, and lack a substituent on C-1.

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S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (99871) 120 64 75, e-mail: root@icps.org.uz. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 504-505, November-December, 2004. Original article submitted June 14, 2004.

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