TABLE 1. Chemical Shifts of the Carbon Atoms in the $^{13}$C NMR Spectra of Codonopsinine (I) and Codonopsine (II), $\delta$, ppm, Py-$d_5$, 0 - TMS

<table>
<thead>
<tr>
<th>Compound</th>
<th>C-2</th>
<th>C-3</th>
<th>C-4</th>
<th>C-5</th>
<th>C-6</th>
<th>C-7</th>
<th>C-8</th>
<th>C-9</th>
<th>C-10</th>
<th>C-11</th>
<th>C-CH$_3$</th>
<th>N-CH$_3$</th>
<th>OCH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>86.94</td>
<td>143.50</td>
<td>119.65</td>
<td>184.06</td>
<td>120.64</td>
<td>113.94</td>
<td>159.06</td>
<td>113.94</td>
<td>129.64</td>
<td>13.76</td>
<td>34.56</td>
<td>55.00</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>84.86</td>
<td>143.50</td>
<td>119.65</td>
<td>184.06</td>
<td>120.64</td>
<td>113.94</td>
<td>159.06</td>
<td>113.94</td>
<td>129.64</td>
<td>13.76</td>
<td>34.56</td>
<td>55.00</td>
<td></td>
</tr>
</tbody>
</table>

SUMMARY

An assignment of the signals in the $^{13}$C NMR spectra of the alkaloids codonopsinine and codonopsine has been made on the basis of results of selective heteronuclear resonance experiments.

LITERATURE CITED


GC-MS ANALYSIS OF TOTAL DITERPENE ALKALOIDS FROM ROOTS OF Aconitum septentrionale

E. G. Sirottenko, Ya. V. Rashkes, and V. N. Plugar'

For the first time, using a MS 25RF chromato-mass spectrometer with a Carlo Erba 5160 chromatograph and a packed column, the possibility of the partial separation of the mixture of diterpene alkaloids of various types from the roots of Aconitum septentrionale has been shown. From their chromatographic parameters and mass-spectral characteristics 18 bases have been detected, including a new one with $M^+$ 407 which was probably deoxydelcorine, while 6-O-methyldelcorine and 6-O-methyleldelidine have been found in plants for the first time.

We have described a procedure for the qualitative and quantitative analysis of the mixtures of diterpene bases from two species of plants of the genus Aconitum [1]. It appeared of interest to confirm the presence of the predicted bases in the same mixture by chromat-mass spectrometry. There is no information on the gas-chromatographic behavior of the diterpene bases.

We set ourselves a dual aim: together with the solution of the concrete problem of the analysis of plant material, to determine the possibility of using the GC-MS method for the identification of diterpene alkaloids of various types. Having prepared equimolar solutions of standard samples of songorine (I), talatisine (II), lappaconine (III), 10-hydroxylappaconine...
(IV), lappaconidine (V), eldeline (VI), lycoctonine (VII), and delphatine (VIII), we made up various combinations of standard mixtures of them and selected conditions for their GC separation.

Figure 1a, shows a chromatogram of a mixture of equal volumes of solutions of (I), (II), (III), (V), (VI), and (VII) (standard 1), which contains four peaks. Analysis of the mass spectra of the corresponding chromatographic peaks (CPs) showed that the C20 bases songorine and talatisine appeared in the first (CP 1) in unseparated form. Lappaconidine and eldeline were not separated under the given conditions (CP 3). Lappaconine (CP 2) and lycoctonine (CP 4) were separated completely from the other components of this mixture.

A combination of the standard solutions of the compounds (standard 2) characteristic for Aconitum plants gave the chromatogram shown in Fig. 1b. This indicated the incomplete separation of the C18 bases lappaconine (CP 1), 10-hydroxylappaconine (CP 2), and lappaconidine (CP 3). On the other hand C19 bases similar in structure - delphatine and lycoctonine (CP 4 and 5) - were separated completely. The incompleteness of the separation found its reflection in the corresponding mass spectra: in each of them the peaks of ions characteristic of the compounds of neighboring CPs were present.

Figure 1c, shows a chromatogram of the unsaponified total alkaloids from the roots of Aconitum septentrionale gathered in the Arkhangelsk oblast in the fruit-bearing period (Σ1). The reason for the poor separation is obviously the thermal decomposition of the ester alkaloids (lappaconitine, N-deacetyllyapponitine, lycaconitine, etc. [1]), which were present in large amounts in this sample. Nevertheless, we attempted to estimate the qualitative composition of the combined material by using known laws of the fragmentation of diterpene bases and the results of the paper cited [1].

To CP 1 (Fig. 1c) corresponded a mass spectrum in which the 100% peak was that of the M+ ion with m/z 327, the fragmentation of which took place in the same way as for M+ of the C20 alkaloid hetisine [2], and the composition of which differed from the latter by two hydrogen