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MASS-SPECTROMETRIC FRAGMENTATION OF PHOSPHORYLATED ANABASINE DERIVATIVES

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The mass-spectrometric fragmentation of hexyl anabasinoisopropyl, and isoamyl anabasinobut-2-ynyl phenylphosphonates has been investigated. Schemes for the fragmentation of the substances are given.

To identify and analyze a trace amount of pesticides, together with other physical methods, wide use is being made of mass spectrometry [1-3]. In order to determine the laws of the fragmentation of organophophorus compounds which assist in the detection of the products of metabolism in the soil and biological materials, we have investigated the mass-spectrometric fragmentation of the previously synthesized hexyl anabasinoisopropyl and isoamyl anabasinobut-2-ynyl phenylphosphonates, which possess biological activity [4].

The fragmentation of the molecular ion depends on the nature both of the substituents at the central phosphorus atom and of the heterocycle itself especially anabasine [5-7].

The peak of the molecular ion of hexyl anabasinoisopropyl phenylphosphonate (Fig. 1) possesses a medium intensity. The mass spectrum of this compound also contains the signal of the $[M - H]^+$ ion obtained by the elimination of one hydrogen atom from the heterocyclic system. The intensity of this ion [*m/z* 443 (1.0)] is less than that of the molecular ion, although in a study of the mass-spectrometric fragmentation of anabasine itself the opposite results were obtained [8a].

The fragmentation of the molecular ion proceeds in various directions. Thus, as the result of the cleavage of a C-C bond in the anabasinopropyl part of the molecule an ion with *m/z* 202 is formed which possesses a high intensity. The formation of such ammonium ions has been reported previously [8b]. When the positive charge is retained in the phosphorus-containing part of the molecule, such cleavage leads to a low-intensity fragment - the hexyl vinyl phosphonate (*m/z* 268) — and protonated vinyl phenylphosphonate (*m/z* 185).

Cleavage of the bond between the piperidine nitrogen atom of anabasine and the α-carbon leads to the ion of hexyl propen-2-yl phenylphosphonate (*m/z* 282), possessing a fairly high intensity. Subsequently, this fragment is converted into the ion of propen-2-yl phenylphosphonate (*m/z* 198). Because of the cleavage of the C-O bond in the fragment split out from the molecule of the substance, pairs of ions are formed. The peaks of the nitrogen-containing ions (*m/z* 175 and 202) possess high intensities.

The phosphorus-containing part forms the ion of the protonated form of hexyl phenylphosphonate (*m/z* 243), which, in its turn, forms the ion of protonated phenylphosphonic acid (*m/z* 159) and an ion with *m/z* 225. These ions and the ion with *m/z* 349 form a dioxophenylphosphorane ion (*m/z* 141).

In contrast to the fragmentation of this compound, in the mass-spectrometric breakdown of isoamyl anabasinobut-2-ynyl phenylphosphonate a comparatively small number of phosphorus-containing ions is formed (Fig. 2). It must be mentioned that in the decomposition of both compounds ions characteristic for the breakdown of the anabasine molecule arise.

The results obtained on the mass-spectrometric fragmentation of phosphorylated anabasine derivatives show that fragmentation of hexyl anabasinoisopropyl phenylphosphonate forms a larger number of phosphorus-containing ions than the breakdown of isoamyl anabasinobut-2-yl phenylphosphonate. The structures of these compounds also differ by the intensities of the ammonium ions formed, especially the ion with *m/z* 175.

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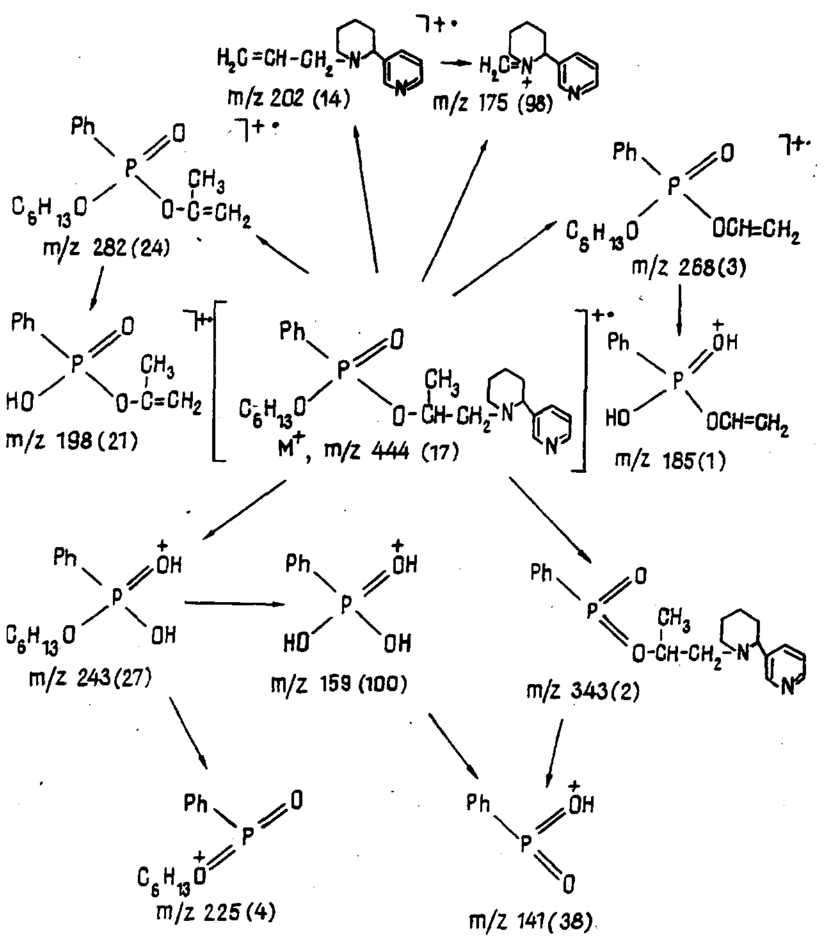

Fig. 1. Mass-spectrometric fragmentation of hexyl anabasinoisopropyl phenylphosphonate.

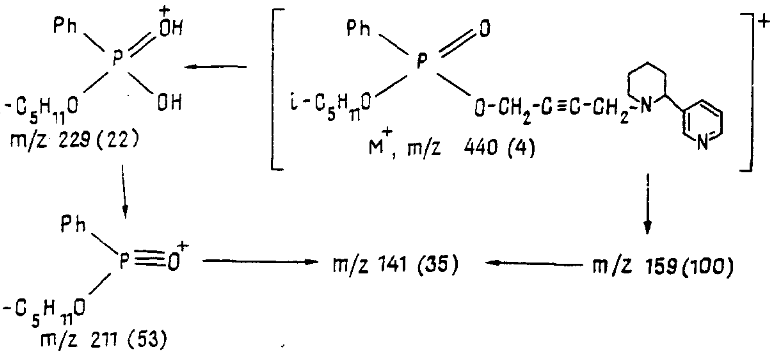

Fig. 2. Mass-spectrometric fragmentation of isoamyl anabasinobut-2-ynylphenylphosphonate.

EXPERIMENTAL

The mass spectra of the compounds were taken on a Varian MAT-311 instrument (USA) with a system for direct insertion at a temperature of the ionizing chamber of 100-120°C and an ionizing voltage of 70 V, an ionizing current of 300 μA, and a temperature of the evaporator of 20-40°C.

Mass spectrum of hexyl anabasinoisopropyl phenylphosphonate, m/z (%):

M^+ 444(17), 445(4.9), 443(0.8), 343(1.9), 326(3), 311(1.3), 310(2.1), 283(4), 283(24.3), 269(1.7), 268(3.3), 203(30), 202(98), 201(52.9), 200(5.9), 199(6), 198(21.4), 190(2.8), 189(17.3) 188(3), 187(15.7), 186(1.7), 185(1.1), 177(2.1), 176(17.1), 175(98), 174(3.8), 173(14.3), 172(2.4), 171(3), 170(3.2), 162(9.9), 161(60), 160(22.9), 159(100), 158(5.4), 157(2.6), 148(2.7), 147(3.9), 146(10) 145(8.7), 144(4.2), 142(8), 141(38.6), 134(3.3), 133(10.6), 132(32), 131(8.8), 126(2.9), 125(8), 124(21.4), 123(5.1), 122(2.4), 121(4.1), 120(21.4), 119(15.7), 118(17.1), 117(8.9), 112(2), 111(3.7), 110(8), 109(2.4), 108(2), 107(5.4).

Mass spectrum of isoamyl anabasinobut-2-ynyl phenylphosphonate,

M^+ 440(4.4), 441(1.4), 439(1), 369(1.9), 299(2.1), 231(1), 230(4.6), 229(22.5), 214(3.2), 213(11.2), 212(28.7), 211(53), 199(2.9), 198(2), 197(4.1), 196(1), 189(0.6), 188(1.4), 187(9.1), 186(4.9), 185(22.5), 184(6.8), 183(6.5), 175(2.6), 173(3.4), 172(3), 171(4.2), 170(6.1), 169(3.2), 163(2.1), 162(26.2), 161(98), 160(15), 159(100), 158(6.1), 157(4.2), 156(5.4), 142(6.2), 141(35), 135(2), 134(10), 133(9.8), 132(8.6), 131(8.5), 130(7.3), 129(2.6), 128(2), 125(4.6), 124(2.2), 121(4.8), 120(16.2), 119(13.7), 118(13.7), 117(6), 107(8.8), 106(18.7), 105(17.5), 104(7.2), 99(2.5), 98(8.5), 94(9.2), 93(6.2), 92(10.8).

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