MASS-SPECTROMETRIC INVESTIGATION OF SOME INDOLE DERIVATIVES

P. V. Sergeev and V. G. Manusadzhyan

UDC 543.51;547.757

The mass spectra of 5-hydroxytryptophan, 5-hydroxytryptamine, 5-methoxy-N-methyltryptamine, 5-hydroxydimethyltryptamine, 5-hydroxyindolylacetic acid, and 5-methoxytryptamine are examined. Schemes for the disintegration of the molecular ions are given.

It is well known that tryptophan undergoes metabolic transformation in living organisms involving oxidation at C_4 followed by decarboxylation, deamination, reoxidation, methylation of the nitrogen in the side chain, etc. The identification of all of the products of the transformation by preliminary chromatography on paper or in a thin layer is a laborious task in some cases, and the development of methods that make it possible to establish the structure of a substance in a spot under investigation is therefore a practical necessity.

In the present paper we set forth the results of a mass spectrometric analysis of chemically pure substances: 5-hydroxytryptophan, 5-hydroxytryptamine, 5-methoxy-N-methyltryptamine, 5-hydroxydimethyltryptamine, 5-hydroxyindolylacetic acid, and 5-methoxytryptamine.*

Mass Spectrum of 5-Hydroxytryptophan (Fig. 1, No. 1)

All of the observed peaks are readily interpreted proceeding from the structural formula: m/e 174 as the ion from the decarboxylation of M^+, subsequent deamination of which during protic rearrangement will lead to peaks 158-161; β-disintegration forms the peak with m/e 145, while γ-disintegration will lead to a peak of weak intensity with m/e 131. Elimination of hydrogen cyanide from the latter ion or of carbon monoxide from the ion with m/e 145 apparently leads to the appearance of an ion with m/e 117. In the first case, subsequent dehydroxylation will lead to the appearance of a peak with m/e 100. The peaks with m/e 91 and 77 should apparently be assigned to the tropylium and benzyl ions.

All of the peaks in the spectra (Fig. 1, Nos. 1-6) with m/e 77, 91, 100, 117, 145, and 146 are similarly interpreted. The remaining peaks are characteristic for each hydroxyindole derivative.

Mass Spectrum of 5-Hydroxytryptamine Creatinine Sulfate (Fig. 1, No. 2)

The preparation is very volatile, and the spectra are readily obtained at room temperature. On sublimation, the substance is apparently readily decomposed to 5-hydroxytryptamine and creatinine sulfate. No peaks are observed above m/e 176. The molecular ion is quite well stabilized.

The intense peaks with m/e 112 and 113 should probably be assigned to creatinine, the molecular weight of which is 113. These peaks are absent in the remaining spectra; the peak with m/e 84 can similarly be assigned to creatinine from which carbon monoxide has been eliminated.

*We thank Professor N. N. Suvorov for supplying the samples.

N. I. Pirogov Second Moscow Medical Institute, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1357-1358, October, 1973. Original article submitted May 3, 1972.

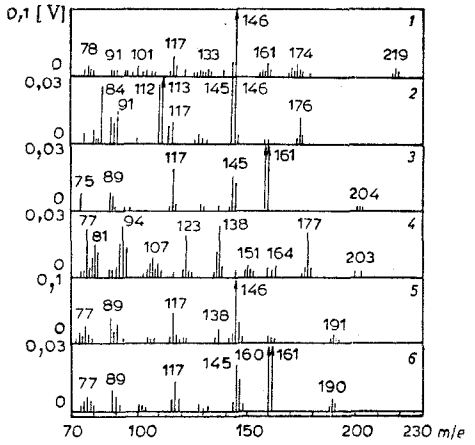

Fig. 1. Mass spectra: 1) 5-hydroxytryptophan (t 150°); 2) 5-hydroxytryptamine (22°); 3) 5-methoxy-N-methyltryptamine (22°); 4) 5-hydroxydimethyltryptamine (50°); 5) 5-hydroxyindolylacetic acid (80°); 6) 5-methoxytryptamine (40°).

Mass Spectrum of 5-Methoxy-N-methyltryptamine (Fig. 1, No. 3)

Peaks [M^+ and $(M-1)^+$] of weak intensity with m/e 204 and 203 and very intense peaks with m/e 160/161 are characteristic for this compound. Despite the fact that the hydrochloride salt of this preparation was investigated, the mass spectra are quite reproducible. The disintegration reaction leading to the appearance of peaks with m/e 160/161, which are also observed for 5-methoxytryptamine, is realized at the C–N bond.

Mass Spectrum of 5-Hydroxydimethyltryptamine (Fig. 1, No. 4)

The mass spectrum of this substance differs from the spectra of the rest of the compounds in that it does not contain hydroxyindole lines with m/e 145/146. A peak with m/e 177 is formed from the molecular ion on loss of a molecule of acetylene. It is more difficult to explain the remaining lines if one proceeds from the structure of the primary ion. Opening of the pyrrole ring, elimination of a C_2NH_3 radical, and migration of hydrogen atoms from the side chain apparently occur. Subsequent elimination of a radical and methane gives peaks with m/e 123, 107, and 94.

Mass Spectrum of 5-Hydroxyindolylacetic Acid (Fig. 1, No. 5)

Even when one considers the two primary directions of disintegration of the products of tryptophan exchange – with retention of the indole ring and with opening of the pyrrole ring – it is quite difficult to explain the origin of the line of the spectrum of 5-hydroxyindolylacetic acid. Elimination of CO_2 or COOH from M^+ will lead to the appearance of peaks with m/e 147 and 146, from which peaks with m/e 138 and 139 are apparently formed.

Mass Spectrum of 5-Methoxytryptamine (Fig. 1, No. 6)

In analogy with the material stated above, one can interpret the mass spectrum of 5-methoxytryptamine as follows: the indole ring is well stabilized, and the methoxy group can lose a methyl group.

Thus, the mass spectra of all of the investigated substances contain peaks with m/e 117, 145, and 146 and molecular peaks of weak intensity. The mass spectra of methoxyindoles additionally contain peaks with m/e 160 and 161. Only the mass spectrum of 5-hydroxydimethyltryptamine differs from the rest of the spectra in that it has a number of characteristic peaks of high intensity with m/e 123, 138, and 177.

In the experiments, the temperature was varied from 50 to 150°. The optimum temperatures and mass spectra for each derivative are presented in Fig. 1. Direct introduction of the substance into the furnace source of an apparatus of the MI-1305 type, as modified by us [1], was used. The ionization potential was 70 V. The input resistance of the electrometric cascades was $5 \cdot 10^{11}$ Ω. The mass spectra of indoles were described in [2].

LITERATURE CITED

1. P. V. Sergeev, V. G. Manusadzhyan, R. D. Seifulla, and M. M. Mul'tanovskii, Arm. Khim. Zh., 24, 99 (1971).
2. A. A. Polyakova and R. A. Khmel'nitskii, Mass Spectrometry in Organic Chemistry [in Russian], Khimiya, Moscow (1972), p. 211.