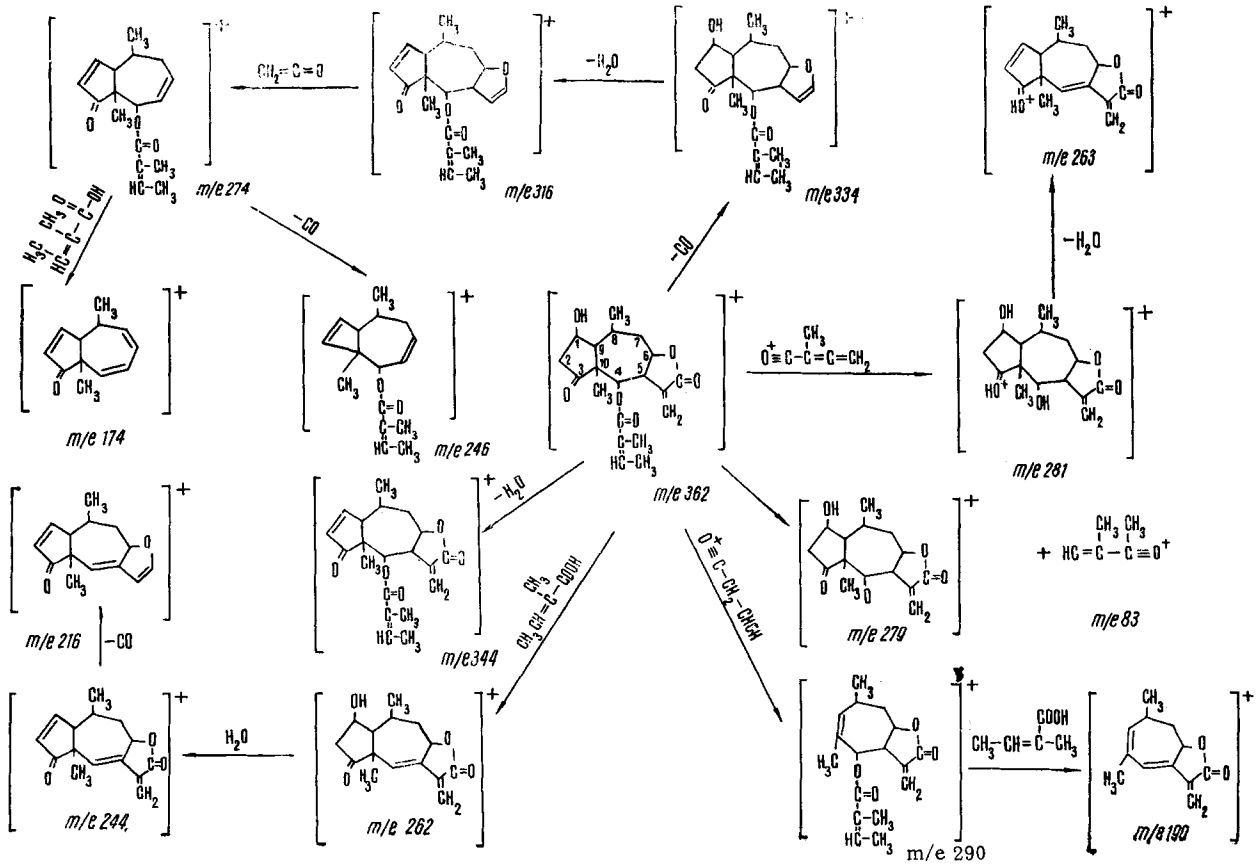
A MASS-SPECTROMETRIC STUDY OF ARNIFOLIN, A NEW SESQUITERPENE LACTONE FROM Arnica montana AND A. Foliosa

P. I. Zakharov, R. I. Evstratova, and K. S. Rybalko

UDC 543.51+547.985

The structure of arnifolin, isolated from Arnica montana L. and A. foliosa Nutt. has been established previously [1, 2].

We have obtained the mass spectrum of this compound and its deutero analog (Fig. 1a and b) and have also proposed a scheme for the decomposition of arnifolin under the action of electron impact.



The mass spectrum of arnifolin contains the low-intensity peak of the molecular ion. The initial stage of the fragmentation of the substance obtained is, as shown by the scheme, the decomposition of the molecular ion in several parallel, competing, directions. The fragment with m/e 344 is formed by the splitting out of a molecule of water from the molecular ion. The presence of a lactone carbonyl group in the arni-

All-Union Scientific-Research Institute of Medicinal Plants. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 587-590, September-October, 1971. Original article submitted March 2, 1971.

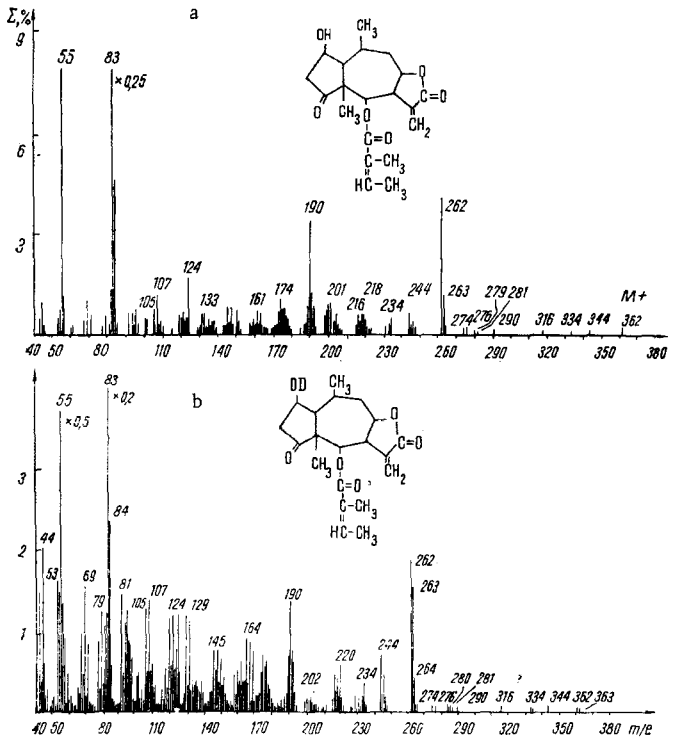


Fig. 1. Mass spectra of arnifolin (a) and [D]arnifolin (b).

folin molecule leads to the ejection from the molecular ion of a CO group, in consequence of which the lactone ring is converted into a dihydrofuran ring and a fragment appears with m/e 334. The loss of a molecule of water by the ion with m/e 334 and of a CO group by the ion with m/e 344 gives one and the same fragment with m/e 316. The presence in the mass spectrum of arnifolin of a fragment with m/e 290 can be explained by the cleavage of bonds 1–9 and 3–10 in the molecular ion.

As a result of the cleavage of the ester bond with and without the transfer of two hydrogen atoms from the tiglic acid to the ester and carbonyl atoms, fragments with m/e 281 and 279 arise. The second process takes place intensively, giving a very strong peak in the mass spectrum of arnifolin with m/e 83, which shows the considerably greater probability of the localization of the positive charge in the cleavage of the ester bond on the acyl residue than on the fragment with m/e 279.

The high intensity of the ion with m/e 84 shows that in the cleavage of the ester bond the transfer of hydrogen also takes place in the reverse direction: from the nucleus of the molecule to the acyl residue. The positive charge is localized only on the acyl, in consequence of which there is no fragment with m/e 278.

The tiglic acid, on being split off from the molecular ion, forms an ion with m/e 262, and on being split off from the fragment with m/e 344 it forms a fragment with m/e 244. The cleavage of the dihydrofuran ring in the fragment with m/e 316 leads to a fragment with m/e 274, which, losing a CO group or tiglic acid, gives an ion with m/e 246 or 174, respectively. The loss of tiglic acid by the ions with m/e 316, 290, and 246 leads to the appearance of fragments with m/e 216, 190, and 146, respectively.

Thus, the mass spectrum of arnifolin agrees well with the structure proposed for it, and its main fragments are due to the presence in the molecule of an alcoholic hydroxy group, a tiglic acid residue, and the carbonyl of the lactone ring.

EXPERIMENTAL

Preparation of [D]Arnifolin. A mixture of 0.05 g of arnifolin and 1 ml of CH_3OD was boiled in the water bath under reflux for 2 h. The solvent was evaporated off. The mass spectrum was taken on an MKh-1303 instrument at 107°C with an ionizing voltage of 50 V using an inlet system providing for the introduction of the sample into the ion source.

Deuteration took place to the extent of 40% (by mass spectrometry).

SUMMARY

The mass spectra of arnifolin and [D]arnifolin have been obtained, and the fragmentation of arnifolin under the action of electron impact has been studied.

A scheme of the fragmentation of arnifolin explaining the main peaks in its mass spectrum has been put forward. The mass spectrum agrees well with the structure established for this substance.

LITERATURE CITED

1. K. S. Rybalko, E. A. Trutneva, and P. N. Kibal'chich, Aptechnoe Delo, 1965, No. 4, 32.
2. R. I. Evstratova, V. I. Sheichenko, K. S. Rybalko, and A. I. Ban'kovskii, Khim.-Farmats. Zh., 3, No. 9, 39 (1969).