

On the basis of results obtained previously [1], the probable structure of 3-hydroxy-6-oxooxoleana-9(11),12(13)-diene-29-oic acid was put forward for isomeristotropic acid. Isomeristotropic and meristotropic acids [2] have identical arrangements of the carboxy, hydroxy, and carbonyl groups in the molecule but differ from one another in the positions of the double bonds. The carbonyl groups in isomeristotropic, meristotropic, and hydroxymeristotropic acids [3] have circular dichromism curves identical in shape and in sign and, therefore, in all these acids they occupy the same positions. The mass spectrum of ethyl isomeristropate (Fig. 1a) has as its strongest peaks those of the molecular ion with m/z 496 (M^+) and of ions with m/z 290 a', 207 b, 217 c, and 128. These fragments — 290 ion a and 207 b — may, as has been established by Djerassi et al. [4-7], be obtained in the retro-Diels-Alder cleavage of ethyl meristropate at ring C. The completely analogous ethyl dioxoisomeristropate (Fig. 1b) forms ions with masses of 482 (M^+), 276 a, 207 b, 203 c, and 173. Both the main ions can undergo further fragmentation. The splitting out from the ions a and a' with m/z 290 and 276 of an $(-OOC_2H_5)$ particle gives the ions c and c' with masses of 217 and 203, respectively. The ion with m/z 128 in the spectrum of ethyl isomeristropate is formed by the splitting out from ion b with m/z 207 of 4 CH_3 and H_2O , and in the deoxy derivative an ion with m/z 137 is formed by the splitting out of CH_3 and H_2O from ion b.

A comparison of the values of the ions a, b, c, and others confirms the localization of the double bonds in ring C and of the carbonyl group in ring E, the presence of additional double bonds in ring C not affecting the main fragmentation process but only causing second-degree effects.

The formation of ion c is evidence in favor of structure (I).

In a comparison of the mass spectra of the ethyl esters of isomeristotropic and meristotropic acids and their deoxy derivatives, it was found that they contain a set of peaks with the same mass numbers but different intensities.

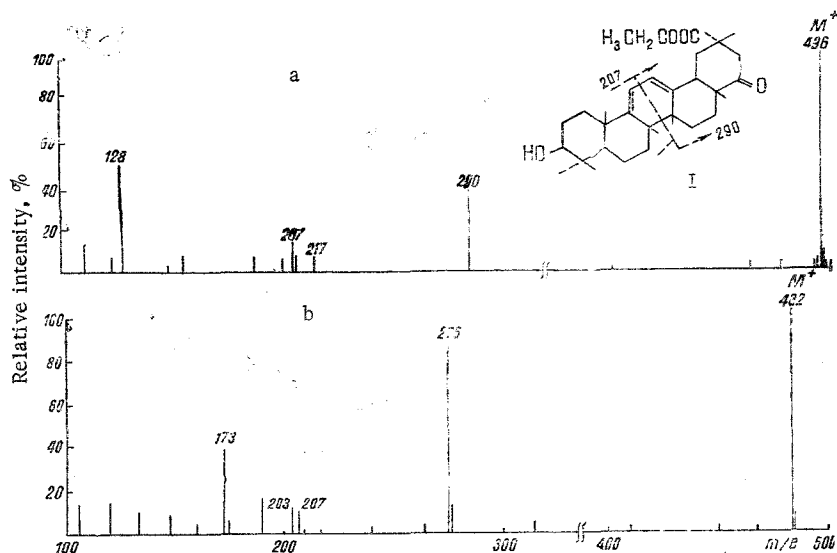


Fig. 1

V. L. Komarov Institute of Botany, Academy of Sciences of the Azerbaidzhan SSR, Baku.
Translated from *Khimiya Prirodnikh Soedinenii*, No. 2, pp. 262-263, March-April, 1982. Original article submitted December 23, 1981.

At the present time the structure and features of the conformation of meristotropic acid have been established definitively [8, 9].

All the results presented, and also the conversion of the diacetate of methyl isomeristropate on oxidation with selenium dioxide into the diacetate or methyl meristotropate, show that the carbonyl group is present in ring E and occupies position 22, as in meristotropic acid.

Thus, isomeristotropic acid is 3-hydroxy-22-oxooleana-9(11),12-diene-29-oic acid and possesses the structure (I).

LITERATURE CITED

1. N. P. Kir'yalov and G. S. Amirova, Khim. Prir. Soedin., 150 (1968).
2. N. P. Kir'yalov and G. S. Amirova, Khim. Prir. Soedin., 87 (1968).
3. G. S. Amirov, Khim. Prir. Soedin., 400 (1981).
4. H. Budzikiewicz, J. M. Wilson, and C. Djerassi, J. Am. Chem. Soc., **85**, 3688 (1963).
5. J. Simonsen and W. C. Ross, The Terpenes, Cambridge University Press (1957).
6. H. Budzikiewicz, C. Djerassi, and D. Williams, Interpretation of Mass Spectra of Organic Compounds, Holden-Day, San Francisco (1964).
7. J. Kapliner and C. Djerassi, J. Org. Chem., **31**, 1945 (1966).
8. A. D. Zorina, L. G. Matyukhina, I. L. Saltykova, and A. G. Shavva, Zh. Org. Khim., **9**, No. 8, 1673 (1973).
9. A. N. Shnulin, G. G. Aleksandrov, Yu. T. Struchkov, Kh. S. Mamedov, and G. S. Amirova, Kristallografiya, **23**, No. 1, 66 (1978).

ALKALOID COMPOSITION OF THE BULBS OF *Crinum amabile*

D. A. Murav'eva and O. I. Popova

UDC 615.322:547.94 (Crinum)

At the present time, 130 alkaloids have been isolated from the plants of the family *Amaryllidaceae* [1-3]. Among them, lycorine and galanthamine have proved to be pharmacologically valuable [4, 5].

We have studied the alkaloids of the hypogeal and epigeal organs of *Crinum amabile* Donn. (*Amaryllidaceae*) introduced into the experimental field of the Transcaucasian zonal experimental station of VILR [All-Union Scientific-Research Institute of Medicinal Plants] at Kobuleti.

In the leaves and roots at the beginning of the vegetation period the total alkaloids amounted to 0.78% and 0.74%, respectively. In the bulbs at the end of the vegetation period (after the first frosts) about 1.56% of combined alkaloids had accumulated.

To isolate the individual alkaloids, the combined alkaloids were extracted from the bulbs with chloroform, and when these were boiled with acetone base (I) separated out with mp 270-272°C, $[\alpha]_D^{20} - 70.6^\circ$ (ethanol), and this was identified as lycorine.

Chromatography on a column of silica gel with elution first by means of benzene and then with benzene-methanol in various ratios gave fractions containing bases (II)-(VII).

Base (II), with mp 208-210°C, $[\alpha]_D + 160^\circ$ (chloroform) was identified by a mixed melting point as tazettine.

Base (III), with mp 127°C, $[\alpha]_D - 122$ (ethanol) proved to be galanthamine.

Base (IV), with mp 184-186°C was identical in its UV and IR spectral characteristics with a racemate of narvedine.

Base (V), with mp 130-131°C $[\alpha]_D - 81.5^\circ$ (ethanol) was identical with galanthine.

Base (VI), with mp 216-217°C, $[\alpha]_D + 160^\circ$ (chloroform), hydrobromide with mp 264°C (decomp.), was identified as hippeastrine.

Pyatigorsk Pharmaceutical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 263-264, March-April, 1982. Original article submitted September 15, 1981.