UDC 547.597+547.918

GAS-CHROMATOGRAPHIC ANALYSIS OF THE SUGARS ENTERING INTO THE COMPOSITION OF NATURAL GLYCOSIDES

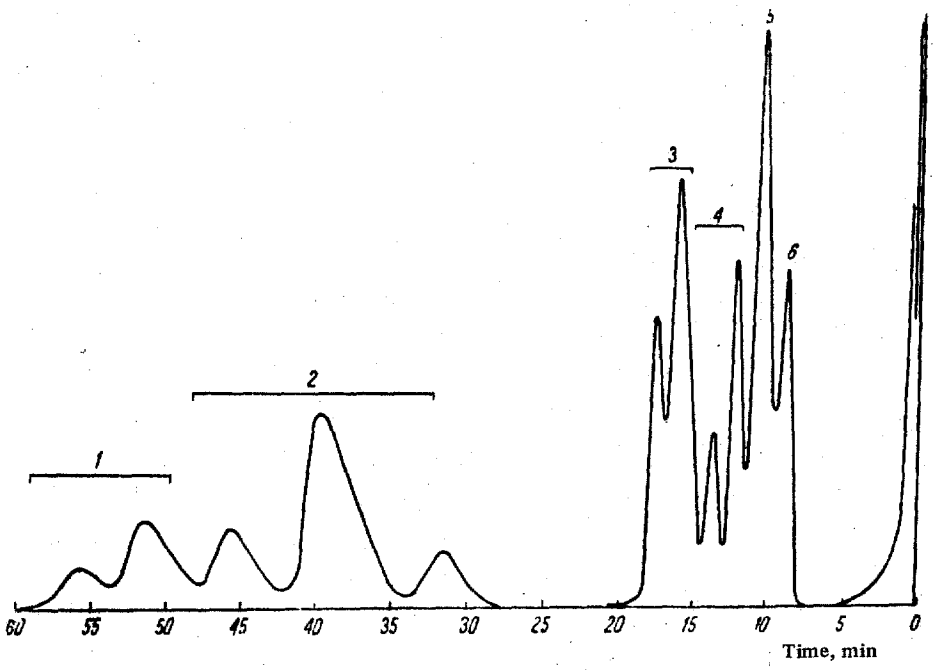
T. T. Gorovits

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 1, pp. 49-50, 1969

The volatility of the sugars themselves is inadequate for gas-chromatographic determinations, and they are analyzed in the form of derivatives. From the point of view of speed of preparation and ease of identification, the trimethylsilyl derivatives of carbohydrates are the most suitable [1].

Sugar	Relative retention time		
L-arabinose	0.16	0.17	0.19
D-xylose	0.28	0.30	—
D-fucose	0.18	0.21	0.24
L-rhamnose	0.18	—	—
D-galactose	0.55	0.68	0.78
D-glucose	0.91	1.00	—

We have separated chromatographically on the nonpolar phase SE-30 a mixture of the sugars found most frequenly in triterpene and steroid (not cardiac) glycosides. In the course of the work it was found that the best separation takes place with the trimethylsilyl derivative not of the sugars themselves but of their methyl glycosides.



Chromatogram of the silylated methyl glycosides of: D-glucose (1), D-galactose (2), D-xylose (3), D-fucose (4), L-rhamnose (5), and L-arabinose (6) (1 : 1 : 1 : 2 : 2 : 1).

To perform the analysis, the individual monosaccharides, and then a mixture of the sugars (50 mg), were methylated at the glycosidic hydroxyl [2]. The methyl glycosides were silylated in pyridine [1] and separated in a UKh-1 chromatogram with a copper column (1 m long and 4 mm in internal diameter) filled with 5% of SE-30 on Celite 545 (40-60 mesh) at a column temperature of 162° C with hydrogen as the carrier gas (36 ml/min). The figure shows a chromatogram of a mixture of six sugars obtained under these conditions.

The individual monosaccharides give several peaks on the chromatogram, each of which corresponds to the presence of a tautomeric form in solution [1]. The relative retention times of the silylated derivatives of the methyl glycosides

of the sugars calculated with respect to silylated methyl α-D-glucopyranoside are given in the table. In the separation of a mixture of sugars, the individual peaks overlap one another, but this does not interfere with qualitative analysis. The results that we have obtained in the gas-chromatographic analysis of the carbohydrate moiety of leontoside B [3] and gypsoside [4, 5] agree with literature data. To establish the molar ratios of the sugars, calibration factors must be determined previously on synthetic mixtures.

REFERENCES

1. C. C. Sweeli, R. Bentley, M. Makita, and D. D. Wells, J. Am. Chem. Soc., 85, 2497, 1963.
2. G. Wullf, J. Chromatogr., 18, 285, 1965.
3. L. G. Mzhel'skaya and N. K. Abubakirov, KhPS [Chemistry of Natural Compounds], 3, 101, 1967
4. N. K. Kochetkov, A. Ya. Khorlin, and Yu. S. Ovodov, Izv. AN SSSR, ser. khim., 83, 90, 1436, 1964.
5. K. Amanmuradov, E. S. Kondratenko, and N. K. Abubakirov, KhPS [Chemistry of Natural Compounds], 1, 143, 1965.

11 July 1968 Institute of the Chemistry of Plant Substances, AS UzSSR

UDC 577.15/17:582.89

COUMARINS OF THE ROOTS OF HERACLEUM ACONITIFOLIUM AND H. PONTICUM

E. D. Giorgobiani and E. P. Kemertelidze

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 1, pp. 50-51, 1969

As already reported [1], we have begun the study of the coumarin composition of species of Heracleum endemic to the Caucasus. In the present paper we give the results of a study of the roots of H. aconitifolium G. Wor. and H. ponticum (Lipsky) I. Manden.

When ethanolic extracts were chromatographed on paper in the petroleum ether–formamide system [2], 9-10 compounds of a coumarin nature were found in the species mentioned.

From the roots of H. aconitifolium we isolated three substances in the crystalline state [3], these being identified as osthole $C_{15}H_{16}O_3$, mp 82-82.5° C; pimpinellin, $C_{13}H_{10}O_5$, mp 117° C; and sphondin, $C_{12}H_8O_4$, mp 192° C.

Osthole and pimpinellin were also obtained from the roots of H. ponticum. In addition, from the latter we isolated isobergapten, $C_{12}H_8O_4$, mp 220° C; and imperatorin, $C_{16}H_{14}O_4$, mp 103° C.

This is the first time that imperatorin has been obtained from the genus Heracleum.

In the species studied, in addition to the coumarins isolated, we identified by paper chromatography isopimpinellin, psoralen, bergapten, and others.

REFERENCES

1. E. D. Giorgobiani, I. F. Komissarenko, and E. P. Kemertelidze, KhPS [Chemistry of Natural Compounds], 4, 47, 1968.
2. N. F. Komissarenko, I. G. Zoz, V. T. Chernobai, and D. G. Kolesnikov, Biokhim., 26, no. 6, 980, 1961.
3. D. G. Kolesnikov, N. F. Komissarenko, and V. T. Chernobai, Med. prom. SSSR, no. 6, 32, 1961.

24 April 1968 Kutateladze Institute of Pharmacological Chemistry, AS Georgian SSR