FORMATION OF GYPSOGENIC ACID ON THE HYDROLYSIS OF GYPSOGENIN GLYCOSIDES

Zh. M. Putieva, E. S. Kondratenko,
and N. K. Abubakirov

UDC 547.918+547.914.4

The lability of gypsogenin glycosides, which is due to the presence of an aldehyde group in the aglycone, has been observed repeatedly [1, 2]. It is rarely possible to obtain the native genin by the acid hydrolysis of such glycosides and most frequently a mixture of products has been obtained [2] of which, so far, only gypsogenin lactone has been identified [1]. In order to avoid these difficulties in the investigation of gypsogenin glycosides, a method has been proposed for their previous conversion into hederagenin glycosides by reduction with sodium tetrahydroborate [2].

We have performed the hydrolysis of the total triterpene glycosides of the roots of *Acanthophyllum gypsophiloides* Rgl. with 5% sulfuric acid. The precipitate of sapogenins that deposited was chromatographed on a column of silica gel in the ethanol—chloroform (25:1) system, and in addition to gypsogenin and gypsogenin lactone, we isolated gypsogenic acid, $C_{30}H_{46}O_5$, mp 375-380°C (decomp.), $[\alpha]_D^{20}$ +100.3±2° (c 0.977; methanol).

Somewhat earlier, V. N. Belous and A. A. Ryabinin [3] isolated gypsogenic acid from the products of the acid hydrolysis of a methanolic extract of the roots of *A. gypsophiloides* and *A. subglabrum*. They considered that this acid was present in the plant itself. We later detected a native glycoside of gypsogenic acid in *A. paniculatum* [4]. However, in a careful investigation of *A. gypsophiloides* we have established that it does not contain glycosides of this acid. Hence, it follows that the appearance of gypsogenic acid is due to its formation in the process in the acid hydrolysis of the gypsogenin glycosides contained in *A. gypsophiloides*. To check the hypothesis put forward, we have hydrolyzed with 5% sulfuric acid the individual acanthophyllosides B and C obtained previously [5]. In both cases, after chromatographic separation of the mixture of sapogenins that had precipitated, together with gypsogenin and its lactone we isolated a certain amount of gypsogenic acid.

It is obvious that in this case this acid is an artifact. It could be formed as the result of the oxidation of the carbonyl group of gypsogenin in the hydrolytic cleavage of the glycosides. The tendency to the autooxidation of an aldehyde group attached to a tertiary carbon atom has been reported previously in a study of the autooxidation of strophanthidin [6].

LITERATURE CITED

1. A. Ya. Khorlin, Yu. S. Ovodov, N. K. Kochetov, Zh. Obshch. Khim., 32, 782 (1962).
2. V. N. Luchanskaya, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 434 (1970).
3. V. N. Belous, and A. A. Ryabinin, Khim. Prir. Soedin., 95 (1967).
4. Zh. M. Putieva, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 104 (1974).
5. Zh. M. Putieva, L. G. Mzhel'skaya, T. T. Gorovits, E. S. Kondratenko, and N. K. Abubakirov, Khim. Prir. Soedin., 177 (1975).
6. M. B. Gorovits, F. S. Khristulas, and N. K. Abubakirov, Zh. Obshch. Khim., 31, 1381 (1961).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 236-237, March-April, 1979. Original article submitted December 11, 1978.

0009-3130/79/1502-0206$07.50