MILD METHOD OF OBTAINING FULLY METHYLATED TRITERPENE GLYCOSIDES

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In spite of the fact that existing methods of methylation are being used successfully to establish the structure of carbohydrate-containing biopolymers, the search for new and more effective methods of methylation is continuing. Thus, recently, Ohno et al., have reported a new method of methylating alcoholic hydroxy groups [1]. We have shown that Ohno's method with small modifications can be applied to the preparation of fully methylated triterpene oligosides.

For methylation we took the methyl ether of a triterpene glycoside — cauloside B — hederagenin 3-O-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside, which has been isolated from the leaves of the Far Eastern plant *Caulophyllum robustum* Maxim. [2]. To perform the reaction in a homogeneous medium, as the solvent we selected dioxane. Diazomethane was used in the form of an ethereal solution. Activated silica gel was added to the reaction mixture in portions. The mixture was stirred at room temperature for 2 h, and then the silica gel was filtered off and the filtrate was evaporated to dryness. The products of partial methylation obtained in this way evaporated to dryness. The products of partial methylation obtained in this way were dissolved in diethyl ether, and gaseous diazomethane was passed through the solution. After the addition of silica gel, the reaction mixture was stirred at room temperature for 5 h. The usual working up gave fully methylated cauloside B with mp 112-115°C, $[\alpha]_D^{18}$ 31.5° (c 0.267; $CHCl_3$). Yield 80%. The product of complete methylation of the aglycoside obtained in this way was identical in its constants with the compound that we synthesized by the methylation of cauloside B using Hakomori's method [3]. The fully methylated derivative of the glycoside from desulfated asterosaponin P isolated from the starfish *Patiria pectinifera* [4] was obtained similarly.

Thus, the modified Ohno method can be used to obtain completely methylated triterpene oligosides.

LITERATURE CITED

1. K. Ohno, H. Nishiyama, and H. Nagase, Tetrahedron Lett., 45, 4405 (1979).
2. N. S. Chetyrina and A. I. Kalinovskii, Khim. Prir. Soedin., 174 (1979).
3. S. Hakomori, J. Biochem. (Tokyo), 55, 205 (1964).
4. A. A. Kicha, in: Abstracts of Lectures at the 5th Molodezhnoe Conference on Synthetic and Natural Physiologically Active Compounds [in Russian], Erevan (1980), p. 49.

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