TRITERPENE GLYCOSIDES OF *Zygophyllum eichwaldii* C.A.M.

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Plants of the *Zygophyllum* genus contain biologically active substances. Aqueous extracts of the epigeal part of *Zygophyllum gaetulum* growing in the Moroccan Sahara are used locally as antispasmolytic, antieczemic, and antidiabetic medicine and for stomach and liver diseases [1].

We studied roots of *Z. eichwaldii* for content of triterpene glycosides.

Ground air-dried material was exhaustively extracted with CH_3OH at 70°C for 2 h. TLC monitoring used $CHCl_3$—CH_3OH—H_2O (65:28:5, 1; 70:23:4, 2). TLC of the methanol extract using systems 1 and 2 detected at least 12 triterpenes that we called arbitrarily glycosides A, B, C, D, E, F, G, H, I, J, K, and L.

The extract was concentrated and dissolved in water. The insoluble part was filtered off. The aqueous solution was treated successively with $CHCl_3$ and butanol. The butanol extract was evaporated and repeatedly chromatographed on KSK silica-gel columns using the abovementioned systems. Three compounds, glycosides C, E, and I, were isolated pure.

Acid hydrolysis of glycosides C and E by H_2SO_4 (5%, 5 h, 90°C) showed (TLC, $CHCl_3$—CH_3OH, 25:1) that their aglycones are identical whereas the carbohydrate part (TLC on plates impregnated with 0.3 M NaH_2PO_4, butanol—methanol—water, 5:3:1) includes arabinose (C) and arabinose and glucose (E).

The PMR spectrum of glycoside E contains seven signals for the protons of seven methyls at δ 0.92-1.72 ppm. The carbohydrate signals of these same groups appear in the ^{13}C NMR at δ 15.35-27.96 ppm. The signal for the olefin proton on C-12 resonates at δ 5.57 ppm; signals for C-12 and C-13, which have a double bond, are observed in the ^{13}C NMR at δ 128.15 and 139.97 ppm. This is characteristic of ursene triterpenoids [2].

Comparison of the ^{13}C NMR of glycoside E with those of various ursene-type compounds found that the aglycone is pomolic acid [3]. Signals at δ 88.49 ppm for C-3 of the genin and 107.28 ppm for C-1 of arabinose indicate that this sugar is bound to the genin through the C-3 hydroxyl. The anomeric proton of arabinose resonates in the PMR as a doublet at δ 4.57 ppm with SSCC J = 5 Hz. This is consistent with the α-configuration for the glycosidic bond. Signals at δ 95.54 and 176.67 ppm in the ^{13}C NMR spectrum correspond to C-1 of glucose and C-28 of the genin, respectively, and suggest attachment of the glucose to the COOH of the aglycone. Therefore, glycoside E is the 28-β-D-glucopyranosyl ester of 3β,19α-dihydroxyurs-12-en-28-oic acid 3-O-α-L-arabinopyranoside.

The ^1H and ^{13}C NMR spectra of glycoside C are almost the same as those of glycoside E. The difference is that signals for glucose are absent in the spectra of compound C and the C-28 signal of pomolic acid resonates at δ 180.36 ppm. Hence, the structure of glycoside C is 3β,19α-dihydroxyurs-12-en-28-oic acid 3-O-α-L-arabinopyranoside.

The spectra and structure of both glycosides were identical to **1** and **2** that were isolated by us from *Sangvisorba officinalis* [4] and *Ilex cornuta* [5].

Glycosides C and E from *Zygophyllum eichwaldii* are isolated for the first time.

Acid hydrolysis decomposes compound I into an aglycone that is identical to the aglycone in glycosides C and E and a carbohydrate part that consists of glucose and galactose. Saponification of glycoside I by 10% NaOH (4 h, 90°C) forms a less polar substance as the progenin (TLC, system 2). This is consistent with the presence of sugar bonded to the aglycone with COOH-group. Therefore, glycoside I is a bisdesmoside.

The poor solubility of the glycoside in water and alcohols, the inability to crystallize it, and the amorphous appearance suggest to us that the molecule contains an inorganic component. Therefore, compound I was solvolyzed [1]. The positive

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reaction of the solvolysis product with $Ba(OH)_2$ solution indicates that the glycoside contains a sulfo-group.

The work on the structure determination of glycoside I is continuing.

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