STRUCTURES OF CALENDULOSIDES G AND H FROM THE ROOTS OF Calendula officinalis

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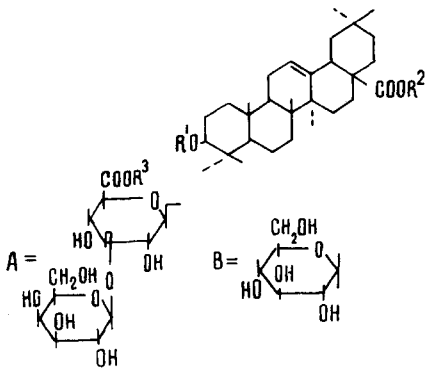
Apart from the glycosides that we isolated previously [1], from the roots of C. officinalis L. by chromatography on a column of silica gel followed by desalting with an anion-exchange resin (Dowex 50 W × 2 100/200, H^+ form) we have obtained the following minor glycosides: calenduloside G, $C_{42}H_{66}O_{14} \cdot 2H_2O$ (I), mp 205-210°C, $[\alpha]_D^{20}+24.1°$ (methanol) and calenduloside H, $C_{48}H_{76}O_{19}$ (II), mp 198-203°C, $[\alpha]_D^{20}+22.1°$ (methanol), and also the monomethyl derivatives of (I), (III), mp 228-230°C and of (II), (IV), mp 222-22 °C.* In the NMR of the acetates of (III), mp 163-165°C, and of (IV), mp 160-162°C, there are signals at 3.68 ppm ($-COOCH_3$) (see formula below).



I. $R^1=A$; $R^2=R^3=H$
II. $R^1=A$; $R^2=B$; $R^3=H$
III. $R^1=A$; $R^2=H$; $R^3=CH_3$
IV. $R^1=A$; $R^2=B$; $R^3=CH_3$

Substances (I) and (II) were identified by TLC with authentic samples of Kasprzyk's glycosides D and C [2] (kindly given to us by Dr. Kasprzyk, Poland). The physicochemical constants of Kasprzyk's glycoside D and C, the position of the bonds, and the configurations of the links of the monomeric residues have not been determined.

When (I) or (II) was heated with 10% HCl in a tube for 7 h, oleanolic acid was formed. In the hydrolyzates, by PC and TLC, D-glucuronic acid and D-galactose were identified in the case of compound (I) and D-glucose, as well, in the case of compound (II).

Elementary analyses and molecular weight determination from the yield of genin showed that compound (I) is a bioside and (II) a trioside of oleanolic acid. On alkaline hydrolysis, (I) remained unchanged, and (II) split into (I) and D-glucose. The acid hydrolysis of the product of the treatment of (I) with diazomethane gave methyl oleanoate, while (II) gave oleanolic acid under the same conditions. When (I) was hydrolyzed with 2.5% H_2SO_4 for 4 h, oleanolic acid 3-O-β-D-glucuronopyranoside was identified. Under the same conditions, compound (II) formed (I), in addition. On partial hydrolysis, in addition to these products, the monomethyl esters of the progenins and of the initial glycosides were identified. Hence, the carbohydrate chains in (I) and (II), consisting of D-glucuronic acid and D-galactose are attached to the hydroxy group, and the D-glucose (II) is attached to the carboxy group of the genin, the D-glucuronic acid being attached directly to the genin.

* Digit is omitted in Russian original – Publisher.

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TABLE 1

Substance	M	$[\alpha]_D$	$[M]_D$	ΔC	Form of the bond
		deg			
Calenduloside H	957,2	+ 22,1	+211,5	+ 11,2	β
Calenduloside G	831,0	+ 24,1	+200,3	+111,7	β
3-O-β-D-glucuronopyranoside [1]	632,8	+ 14	+ 88,6	—	—
Methyl α-D-glucopyranoside [7]	194,2	+149	+289,4	—	—
Methyl β-D-glucopyranoside [7]		− 25	− 48,6	—	—
Methyl α-D-galactopyranoside [7]		+161	+312,6	—	—
Methyl β-D-galactopyranoside [7]		+ 5	+ 9,7	—	—

After the periodate oxidation of (I) and (II), D-glucuronic acid was detected. Consequently, there is a 1 → 3 bond between the glucuronic acid and the D-galactose.

Methylation by Hakomori's method [3] gave the permethylate of (I), $C_{50}H_{82}O_{14}$, mp 102-105°C, $[\alpha]_D^{20}$ +14.3° (methanol). Its reduction with $LiAlH_4$ in dioxane [4] formed the reduced product $C_{48}H_{82}O_{12}$ with mp 118-120°C, $[\alpha]_D^{20}$+12° (methanol), which was remethylated. Methanolysis of the resulting methyl ether gave methyl 2,4,6-tri-O-methyl-D-glucopyranoside and methyl 2,3,4,6-tetra-O-methyl-D-galactopyranoside in a ratio of 1:1 (GLC).

The methylation of (II) gave a permethylate $C_{59}H_{98}O_{19}$, mp 94-96°C, $[\alpha]_D^{20}$ 0° (methanol). The tetrahydroaluminate cleavage of the permethylate (II) formed the same substance as in the reduction of the permethylate (I) and also 2,3,4,6-tetra-O-methyl-D-sorbitol, $[\alpha]_D^{20}$ +12° (ethanol). According to the literature: $[\alpha]_D^{20}$+10.3° (ethanol) [5].

The calculation of the configurations of the glycosidic bonds was performed in accordance with Klyne's rule [6] (Table 1).

The structure of (I) was established as oleanolic acid 3-O-β-D-galactopyranosyl-(1 → 3)-β-D-glucuronoside, and the structure of (II) as the 28-acyl-β-D-glucopyranoside of (I).

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