THE STRUCTURE OF CALENDULOSIDE B FROM THE ROOTS OF Calendula officinalis

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We have previously reported the structure of a monoside and a bioside (calenduloside A) of oleanolic acid isolated from the roots of Calendula officinalis L. [1, 2]. In the present paper we give information to establish the structure of calenduloside B – a trioside of oleanolic acid with mp 232-234° C (methanol), $[\alpha]_D^{20}$ + 57.2° (c 0.5; methanol). Found: mol. wt. 1013 (spectrophotometrically). $C_{48}H_{78}O_{18} \cdot 2\frac{1}{2}H_2O$. Calculated: mol. wt. 988.2.

The acid hydrolysis of calenduloside B gave oleanolic acid, D-glucose, and D-galactose, and stepwise hydrolytic cleavage with 6% H_2SO_4 and alkaline hydrolysis of calenduloside B gave a glycoside identical with calenduloside A – O-β-D-galactopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→3)-oleanolic acid.

The presence in the IR spectrum of an absorption band in the 1740 cm^{-1} region, the formation of oleanolic acid in the hydrolysis of the calenduloside methylated with diazomethane and of the permethylate shows the presence of an ester bond in the molecule.

The acetylation of calenduloside B gave an acetate, $C_{70}H_{100}O_{29}$, with mp 176-178° C (methanol), $[\alpha]_D^{20}$ + 14.3° (c 0.5; chloroform); methylation with methyl iodide in dimethyl sulfoxide in the presence of sodium hydride [3] gave the permethylate $C_{59}H_{100}O_{18}$, with mp 115-117° C, $[\alpha]_D^{20}$ + 28.6° (c 0.5; methanol).

The elementary analyses of calenduloside B, its acetate, and its permethylate corresponded to the calculated figures.

When the permethylate was cleaved with hydrochloric acid, 2,3,4,6-tetra-O-methyl-D-glucopyranose, 2,3,4,6-tetra-O-methyl-D-galactopyranose, and 2,3,6-tri-O-methyl-D-glucopyranose were identified by PC, TLC, and GLC in comparison with authentic samples.

The configuration of the glycosidic bond was determined by Klyne's rule [4] on the basis of the molecular rotation differences between calenduloside B and calenduloside A.

Substance	[M], degrees
Calenduloside A (Mol. wt. 799, $[\alpha]_D^{20}$ + 41.4°)	+330.8
Calenduloside B (Mol. wt. 988.2, $[\alpha]_D^{29}$ +57.2°)	+565.3
Methyl α-D-glucopyranoside [5]	+149
Methyl β-D-glucopyranoside [5]	–25

Thus, calenduloside B is O-β-D-galactopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→3)-oleanoloyl-(28→1) α-D-glucopyranoside. Its complete structure may be represented in the following way:

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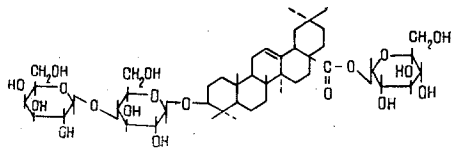

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