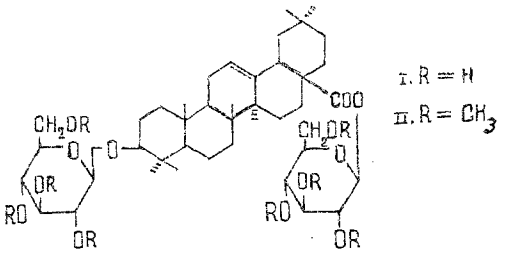

We are the first to have obtained this bisdesmoside from a natural material: It has previously been obtained by partial synthesis from oleanolic acid and α-D-glucopyranosyl bromide benzoate [5]. It must be mentioned that a glycoside close in structure has been isolated from *Anchusa officinalis* L. (Boraginaceae) — anchusoside I, to which the structure of oleanolic acid 28-O-α-D-glucopyranoside 3-O-β-D-glucopyranoside was assigned.

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SYNTHESIS OF ACETYLATED GLYCOSIDES OF 2,3-DIHYDROXY-1,4-NAPHTHOQUINONE

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UDC 547.656+547.455+616—006.6

We have previously reported an autocatalytic method of glycosylating hydroxynaphthoquinones with sugar 1,2-orthoesters [1]. In studying the possibilities of this method, 2,3-dihydroxy-1,4-naphthoquinone (III) [2] was glycosylated with orthoesters of D-glucose (I) [3] and of maltose (II) [4]. Boiling equimolar amounts of (I) and (III) in absolute chlorobenzene for 1 h led to a mixture of (IV) and (V) (20% and 40%, respectively, calculated on the orthoester). The orthoester of maltose (II) reacted completely with an equimolar amount of the quinone (III) in 5 h to form (VI) (48%) and (VII) (32%). The predominant formation of the bisglucoside (V) is apparently due to the electron-accepting effect of the glycosidic radical R_3 of the monoglucoside (IV), which causes an increase in the affinity and nucleophilicity of the neighboring hydroxy group and thereby increases the reactivity of (IV) as compared with the initial quinone (III). When (III) was glycosylated with the orthoester (II), the steric effect of the disaccharide radical R_4 directed the course of the reaction predominantly to the formation of the monomaltoside (VI). Glycosylation by the orthoesters (I) (1 h) and (II) (11 h) at a quinone:orthoester ratio of 1:2 led to mixtures of (IV) (4%) and (V) (83%) and of (VI) (52%) and (VII) (41%), respectively, which also confirms the conclusion that we drew concerning the influence of the radicals R_3 and R_4 on the reactivities of the monoglycosides (IV) and (VI).

The structures of the glycosides (IV-VII) were confirmed by the results of IR and ^1H and ^{13}C NMR spectroscopic studies and of elementary analysis. The signals of the anomeric carbon atoms of a D-glucose residue attached to the aglycone appeared at 98-100 ppm, which shows the β-configuration of the glycosidic bond [1]. All the newly obtained glycosides consisted of light yellow amorphous powders.

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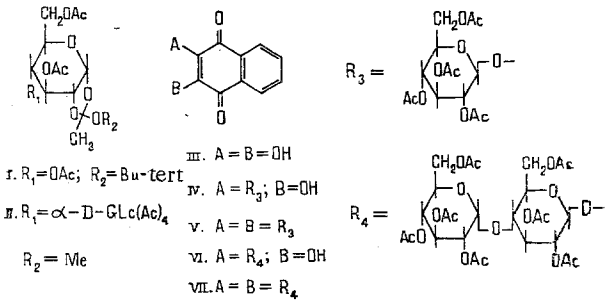

3-Hydroxy-2-(tetra-O-acetyl-β-D-glucopyranosyloxy)-1,4-naphthoquinone (IV), $[\alpha]_D^{20}$ −75.7° (c 1; $CHCl_3$).

2,3-Bis(tetra-O-acetyl-β-D-glucopyranosyloxy)-1,4-naphthquinone (V), $[\alpha]_D^{20}$ −90.7° (c 1; $CHCl_3$).

2-[Tri-O-acetyl-4'-O-(tetra-O-acetyl-α-D-glucopyranosyl)-β-D-glucopyranosyloxy]-3-hydroxy-1,4-naphthoquinone (VI), $[\alpha]_D^{20}$ +80.0° (c 1; $CHCl_3$).

2,3-Bis[tri-O-acetyl-4'-O-(tetra-O-acetyl-α-D-glucopyranosyl)-β-D-glucopyranosyloxy]-1,4-naphthoquinone (VII), $[\alpha]_D^{20}$ +24.0° (c 1; $CHCl_3$).

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INTEGRAL INTENSITIES OF THE IR BANDS OF THE SKELETAL VIBRATIONS OF THE HETEROAROMATIC RINGS OF QUINAZOLINE ALKALOIDS IN THE 1480-1630 cm^{-1} REGION

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We have previously established that the total integral intensity ($\Sigma A \cdot 10^4$, liter·mole^{-1}·cm^{-2}) of the skeletal ν (C=C) bonds of the aporphine and furoquinoline alkaloids possess a selective sensitivity to the electronic interaction of substituents with the nucleus [1, 2].

With the aim of a further study of the specific features of the interaction of the constituents with the π-electrons of the heteroaromatic system, we have measured ΣA values of a number of quinazoline alkaloids. The results obtained are presented in Table 1.

The decrease in ΣA on passing from deoxypeganine (DOP) to peganine (III) is connected with the basicity of the N_1 nitrogen atom.

In deoxyvasicinone (DOV), the integral intensity is almost 1.5 times less than in DOP, which can be explained by the acceptor influence of the carbonyl group on the aromatic system. The weakening of the donor nature of the N_1 nitrogen atom, which forms an intramolecular H bond with the proton of the hydroxy group, leads to a considerable decrease in ΣA for vasicinone (ΣA = 6.50) as compared with DOP (ΣA = 12.90), and DOV (ΣA = 9.20).

It must be mentioned that the value of ΣA in 7-OCH_3-DOV is considerably higher than in the 6-OCH_3 and 8-OCH_3 derivatives. As in the case of substituted quinolines [3-6], the high value of ΣA for 7-OCH_3-DOV is due to the effect of the direct conjugation of the OCH_3 substituent (+C) with the carbonyl group (−C).

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