For this purpose, the methyl ether (I) was treated with 44 equivalents of lithium in the presence of methanol in liquid ammonia at − 70°C, and the methoxydiene (II) was obtained (yield 68%). The hydrolysis of (II) with acetic acid in methanol led to the ketone (III) (yield 70%). The latter, on bromination-dehydrobromination with one equivalent of pyridine bromide-perbromide in pyridine formed the diene (IV), the dehydration of which with HCl in chloroform led to trenbolone (V).

17β-Hydroxyestra-4.9.11-trien-3-one (V): mp 184-186°C. UV spectrum, λ_{max}: 343 nm (log ε 4.41). IR spectrum (ν_{max}^{KBr}, cm^{-1}): 3350 (OH), 1640 (C=O): 1570, 1560, 1540 (C=C). PMR spectrum ($CDCl_3$, δ, ppm 0 − HMDS): 0.91 (s, 3H, CH_3), 3.90, (t, 1H, H-17), 5.78 (s, 1H, H-4), 6.42 and 6.47 (d, 1 H each, 1 H, J = 10 Hz, H-11 and H-12). Mass spectrum (m/z, %): 270 (M^+, 100), 258 (M−H_2O, 26).

The intermediate compounds (III) and (IV) exhibit anabolic effects.

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GLYCOSYLATION OF TRITERPENOIDS OF THE DAMMARANE SERIES.

VIII. DAMMARANE HYDROXYKETONE β-D-GLYCOPYRANOSIDES

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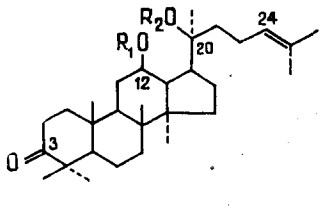
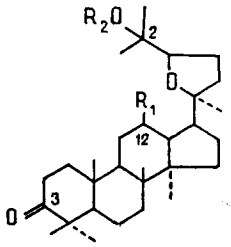
To study structure-activity relationships, we have obtained glucosides from one of the components of the triterpene fraction from birch leaves − 12β,20(s)-dihydroxydammar-24-en-3-one (I) [1] − and also of the 3-ketodammarane alcohols (II) and (III). Glycosylation was





I. R_1=R_2=H
II. R_1=OH; R_2=H
III. R_1=R_2=H
IV. R_1=Glc(OAc)$_4$; R_2=H
V. R_1=H; R_2=Glc (OAc)$_4$
VI. R_1=Ac; R_2=Glc (OAc)$_4$
VII. R_1=OGlc (OAc)$_4$; R_2=H
VIII. R_1=OGlc (OAc)$_4$; R_2=Glc (OAc)$_4$
IX. R_1=H; R_2=Glc (OAc)$_4$

effected with α-acetobromoglucose in the presence of silver oxide by a method described previously [2]. The results are given below (α-ABG − α-acetobromoglucose):

Initial substances, mmole			Reaction products	Recovery of the initial substances, %
hydroxyketone	α-ABG	Ag_2O		
I, (I)	8	3	39.1% (IV): (V) = 3:1	31.5
II, (I)	3	3	59.9% (VII); 9.9% (VIII)	25.0
III, (I)	3	3	13.9% (IX)	75.2

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The interaction of the hydroxyketones (I) with α-acetobromoglucose led to the formation of two monoglucosides, (IV) and (V), which it did not appear possible to isolate in the individual state with the aid of column chromatography. In view of the fact that the tertiary OH group at C-20 does not undergo acetylation under the usual conditions, the mixture of monoglucosides (IV) and (V) was first treated with acetic anhydride in pyridine and was then chromatographed on a column of silica gel. As a result, the monoglucoside (IV) and the product of the acetylation of monoglucoside (V) – compound (VI) – were obtained.

The condensation of 12β,25-dihydroxy-20(S),24(R)-epoxydammaran-3-one (II) with α-acetobromoglucose gave a mixture of the monoglucoside (VII) and the diglucoside (VIII), while the glucosylation of ocotillol (III) gave the monoglucoside (IX).

The glucosides obtained (VII-IX) were isolated with the aid of column chromatography on silica gel in the hexane–acetone system. The individuality of the substances was checked with the aid of TLC in the benzene–chloroform–methanol (6:4:1) and hexane–acetone (2:1) systems.

The elementary analyses of all the newly obtained compounds corresponded to the calculated figures. The structures of the glucosides were confirmed by IR and ^{1}H NMR spectroscopy. The spin-spin coupling constants showed the trans-configuration of the glucosidic bonds in all the glucosides.

The initial hydroxyketones (I-III) were obtained by the oxidation of the corresponding polyols with chromium trioxide in pyridine.

Monoglucoside (IV). Amorphous. $[\alpha]_D^{20}$ +25.5° (c 1.0; chloroform). IR spectrum (ν, cm^{-1}): 1697, 1752, 3454. ^{1}H spectrum (δ, ppm): 0.90 (s, 3H), 0.98 (s, 3H), 1.01 (s, 3H), 1.05 (s, 3H), 1.10 (s, 3H), 1.11 (s, 3H), 1.65 (s, 3H), 1.71 (s, 3H), 2.00 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.09 (s, 3H, OAc), 3.68 (m, 1H, H-5), 3.83 (t-d, 1H, J = 10 Hz, J = 10 Hz, J = 5.0 Hz, H_a-12), 3.94 (s, 1H, OH), 4.22 (d, 2H, J = 4.7 Hz, 2H-6'), 4.75 (d, 1H, J = 7.5 Hz, H-1'), 4.90-5.23 (m, 4H, H-2', H-3', H-4', H-24).

Monoglucoside (VI). Amorphous. $[\alpha]_D^{20}$ −5.8° (c 0.6; chloroform). IR spectrum (ν, cm^{-1}): 1700, 1747. ^{1}H spectrum (δ, ppm): 0.93 (s, 6H), 1.00 (s, 3H), 1.04 (s, 3H), 1.08 (s, 3H), 1.19 (s, 3H), 1.59 (s, 3H), 1.65 (s, 3H), 2.00 (s, 6H, 2 × OAc), 2.03 (s, 3H, OAc), 2.07 (s, 6H, 2 × OAc), 3.67 (m, 1H, H-5'), 4.11 (d, 2H, J - 2.7 Hz, 2H-6'), 4.67 (d, 1H, J = 7.5 Hz, H-1'), 4.84 (t-d, 1H, J = 10.0 Hz, J = 10.0 Hz, J = 5.0 Hz, H_a-12), 4.90-5.20 (m, 4H, H-2', H-3', H-4', H-24).

Monoglucoside (VII). mp 236-238°C (ethanol). $[\alpha]_D^{20}$ +4.0° (c 0.93; chloroform). IR spectrum (ν, cm^{-1}): 1698, 1752, 3535. ^{1}H spectrum (δ, ppm): 0.88 (s, 3H), 0.96 (s, 3H), 0.99 (s, 3H), 1.06 (s, 3H), 1.09 (s, 9H), 1.19 (s, 3H), 2.01 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.08 (s, 3H, OAc), 3.67 (m, 2H, H-5', H_a-12), 3.84 (m, 1H, H-24), 4.12 (d-d, 1H, J = 2.7 Hz, J = −12.0 Hz, H-6'), 4.25 (d-d, 1H, J = 5.0 Hz, J = −12.0 Hz, H-6'), 4.60 (d, 1H, $J_{1',2'}$ = 7.5 Hz, H-1'), 4.92-5.23 (m, 3H, H-2', H-3', H-4').

Diglucoside (VIII). mp 245-247°C (ethanol), $[\alpha]_D^{20}$ −4.8° (c 0.93; chloroform). IR spectrum (ν, cm^{-1}): 1698, 1748. ^{1}H spectrum (δ, ppm): 0.90 (s, 3H), 0.98 (s, 3H), 1.00 (s, 3H), 1.06 (s, 6H), 1.10 (s, 3H), 1.14 (s, 6H), 2.00-2.08 (s, 24H, 8 × OAc), 3.65 (m, 3H, 2 × H-5', H_a-12), 3.84 (m, 1H, H-24), 4.11 (m, 2H, 2 × H-6'), 4.24 (d-d, 2H, J = 4.7 Hz, J = −12.0 Hz, 2H-6'), 4.63 (d, 1H, J = 7.5 Hz, H-1' at C-12), 4.95 (d, 1H, J = 8.0 Hz, H-1' at C-25), 4.90-5.21 (m, 2H-2', 2H-3', 2H-4').

Monoglucoside (IX). mp 185-187°C (ethanol). $[\alpha]_D^{20}$ +29.8° (c 1.0; chloroform). IR spectrum (ν, cm^{-1}): 1696, 1751. ^{1}H spectrum (δ, ppm): 0.90 (s, 3H), 0.96 (s, 3H), 1.01 (s, 3H), 1.04 (s, 3H), 1.08 (s, 3H), 1.09 (s, 3H), 1.13 (s, 3H), 1.19 (s, 3H); 2.00 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.08 (s, 3H, OAc), 3.66 (m, 1H, H-5'), 3.86 (m, 1H, H-24), 4.11-4.23 (m, 2H, 2 × H-6'), 4.85 (d, 1H, J = 8.0 Hz, H-1'), 4.92-5.19 (m, 3H, H-2', H-3', H-4).

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