Synthesis of triterpene 3-*O*-(2-deoxy-α-glycosides)

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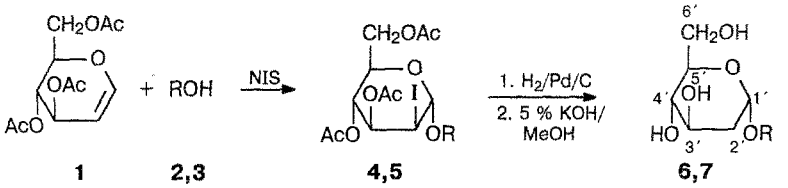
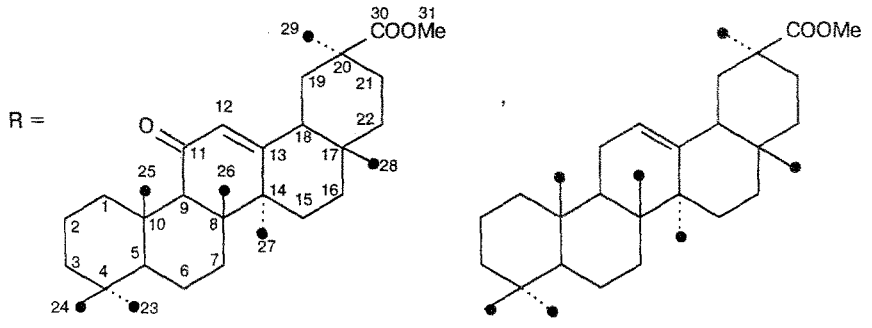
Natural triterpene glycosides are known for their diversified biological activity (antiphlogistic, antitumor, hemolytic, antifungal, antiviral, *etc.*). 2-Deoxyglycosides are synthetic intermediates and common structural units of many biologically active substances.

We synthesized triterpene 3-*O*-(2-deoxy-α-glycosides) (**4—7**) by electrophilic glycosylation of triterpene alcohols with readily accessible D-glycal acetate (**1**) in the presence of N-I-succinimide (NIS).[1]



1 **2,3** **4,5** **6,7**



2,4,6 **3,5,7**

Biologically active triterpenoids of licorice root (*Clycyrrhizae glabra*), *viz.*, methyl 18β-glycyrretate (**2**) and methyl 11-deoxo-18β-glycyrretate (**3**), were used as alcoholic components.

General procedure for preparing glycosides 4 and 5. A mixture of tri-*O*-acetyl-D-glycal **1** (2 mmol) (see Ref. 2) and an equivalent amount of **2** or **3** was dissolved in 50 mL of anhydrous CH_2Cl_2/MeCN (1:1) in the presence of calcined 4 Å molecular sieves, and NIS (2.3 mmol) was added with stirring in the dark. After ~70 h (TLC monitoring), the solvent was evaporated and the residue was extracted with CH_2Cl_2, washed with a 10 % solution of $Na_2S_2O_3$, and dried with $MgSO_4$. Compounds **4** and **5** were isolated by column chromatography on silica gel (ethyl acetate—pentane) in 55—60 % yield. The data of elemental analysis are in satisfactory agreement with the calculated data. IR (Vaseline oil), ν/cm^{-1}: 1760—1750 (OAc), 1730—1720 (COOMe). Hydride abstraction of iodine from the resulting 2-I-glycosides through the action of 10 % Pd/C in ethyl acetate followed by mild deacetylation with a 5% methanolic solution of KOH gave 3-*O*-(2-deoxy-α-D-*arabino*-hexopyranosides) (**6, 7**) in 75—80 % yield. The structures of these compounds were determined by ^{13}C NMR spectra. For example, on going from genines **2** and **3** to glycosides **6** and **7**, the signal of the C(3) atom shifts downfield by 3.7—4.0 ppm. The anomeric C(1′) atoms of the carbohydrate residues are exhibited at 93.4—93.5 ppm, which indicates the formation of an α-glycoside bond.[3]

Glycoside 6: white powder, dec. at 210—212 °C. $C_{37}H_{58}O_8$. $[\alpha]_D^{20}$ +95° (*c* 0.02, $CHCl_3$). UV (MeOH), λ_{max}/nm: 248.2 (log ε 3.74). ^{13}C NMR ($CDCl_3$), δ: 21.7 C(2), 81.7 C(3), 200.5 C(11), 128.5 C(12), 169.5 C(13), 177.1 C(30), 51.9 C(31), 93.4 C(1′), 38.2 C(2′), 71.9 C(3′), 69.2 C(4′), 72.6 C(5′), 62.3 C(6′).

Glycoside 7: white powder, dec. at 214—216 °C. $C_{37}H_{58}O_7$. $[\alpha]_D^{20}$ +83° (*c* 0.05, $CHCl_3$). IR (Vaseline oil), ν/cm^{-1}: 3600—3200 (OH); 1730—1720 (COOMe). ^{13}C NMR ($CDCl_3$), δ: 21.7 (C(2)), 82 (C(3)), 30.0 (C(11)), 122.6 (C(12)), 144.5 (C(13)), 177.8 (C(30)), 51.7 (C(31)), 93.5

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(C(1')), 39.3 (C(2')), 72.0 (C(3')), 69.3 (C(4')), 72.5 (C(5')), 62.2 (C(6')).

References

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Simple catalytic synthesis of 3,3,5-trimethylcyclohexylamine

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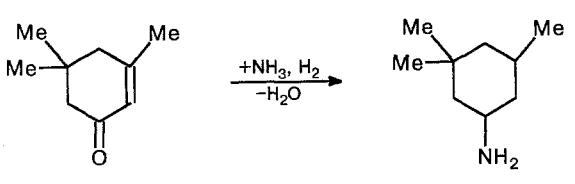
Catalytic inter- and intramolecular hydroamination of aldehydes and ketones occupy a prominent place among the practical methods for preparing amines.[1] A process in which the >C=O and >C=C< groups incorporated in the molecule of a starting carbonyl compound are simultaneously converted into >CH—NH_2 and >CH—CH< groups, respectively, under conditions of hydroamination is of interest from the synthetic viewpoint. In this case, the products of crotone condensation of aldehydes and/or ketones are convenient synthons for the synthesis of amines. We found that in the presence of the copper—zinc—aluminum-containing SNM-1 catalyst, which is used in the industrial synthesis of methanol and is capable of accelerating amination,[2] isophorone (**1**) reacts with hydrogen and ammonia to give 3,3,5-trimethylcyclohexylamine (**2**):



1 **2**

Vapor-phase hydroamination of **1** was carried out in a flow-type reactor with a fixed bed of SNM-1 (30 cm^3). The products were analyzed by GLC (Chrom-5) and identified on a Kratos-MS-25RF/DS-90 GC-mass spectrometer. The reaction of **1** with a hydrogen—ammonia mixture was carried out at a temperature of 210—220 °C, a total pressure of 3.5 MPa, an H_2 : NH_3: **1** molar ratio of 1 : 0.75 : (0.02—0.03), and a specific rate of introduction of **1** of 2.2 mol (h L Cat)$^{-1}$. Under these conditions, the degree of conversion of **1** was more than 99 % (w/w). The major product of the conversion of **1** was 3,3,5-trimethylcyclohexylamine **2**, whose yield was 90—95 % (w/w). Along with amine **2**, 4—6 % (w/w) di(3,3,5-trimethylcyclohexyl)amine (**3**) and 1—3 % (w/w) 1,1,3-trimethylcyclohexane (**4**) were obtained. Secondary amine **3** results apparently from hydrogenation of the Schiff's base formed in the condensation of **1** with **2**, and **4** results from the exhaustive hydrogenation of **1**.

MS, m/z (I_{rel} (%)), compound **2**: 141 $[M]^+$ (11), 116 (16), 114 (7), 109 (18), 85 (9), 84 (92), 83 (20), 82 (7), 71 (12), 70 (100), 69 (13), 68 (11), 67 (10), 57 (16), 56 (20), 52 (27), 53 (7), 44 (38), 43 (76), 42 (24), 41 (50), 40 (6), 39 (23); **3**: 265 $[M]^+$ (4), 250 (9), 209 (7), 208 (40), 195 (7), 194 (42), 89 (7), 70 (22), 69 (19), 57 (8), 55 (20), 45 (48), 44 (100), 43 (27), 42 (7), 41 (27), 39 (7); **4**: 126 $[M]^+$ (2), 112 (10), 111 (100), 83 (29), 70 (20), 69 (95), 68 (6), 67 (12), 57 (15), 56 (32), 55 (60), 53 (10).

Thus, catalytic hydroamination of compound **1** can serve as the effective preparative-scale method for preparing compound **2**.

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