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SYNTHESIS OF NEW C-2 TRIAZOLE-LINKED ANALOGS OF TRITERPENOID PENTACYCLIC SAPONINS

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C-2 mono- and bis-1,2,3-triazole-linked analogs of lupane, ursane, and oleane triterpenoid saponins were synthesized for the first time using regioselective Cu(I)-catalyzed 1,3-dipolar cycloaddition (CuAAC) of peracetylated sugar azides and C-2 propynyl derivatives of triterpene acids. Cytotoxic activity of the synthesized compounds was studied in vitro *at the National Cancer Institute (USA). Several of the synthesized compounds exhibited weak cytotoxic activity.*

Keywords: triterpenoids, betulinic acid, ursolic acid, oleanolic acid, glycosides, 1,2,3-triazoles, 1,3-dipolar cycloaddition.

Saponins are a specific class of broadly distributed plant secondary metabolites, the molecules of which contain a pentacyclic triterpenoid or steroid aglycon called a sapogenin and one or more sugar chains connected at various positions through *O*-glycoside bonds to the hydrophobic polycyclic core. Triterpenoid saponins display a variety of structures and exhibit broad spectra of biological and pharmacological activities such as hemolytic, cytotoxic, anti-inflammatory, antimicrobial, and hypolipidemic [1, 2]. Many natural and synthetic *O*-glycosides of the lupane-, ursane-, and oleane-type have now been synthesized using classical methods to form triterpene C-3 and/or C-28 glycoside bonds [3]. It is assumed that the water-solubility and absorption would be improved; the pharmacological properties of the triterpenoids, enhanced, if hydrophilic sugar residues were bonded to them. An analysis of the structure–activity relationship of many libraries of obtained compounds revealed changes of biological activity even if the chemical structure was slightly altered and a dependence on the types of aglycon, sugar, number of sugar residues in the chains, and positions at which the sugar was bound to the aglycon [3]. Conjugates of pentacyclic triterpenoids and sugars linked through 1*H*-1,2,3-triazole rings were investigated several times [4–6]. Therefore, it seemed interesting to determine how replacing the traditional *O*-glycoside bond by an artificial biologically active 1,2,3-triazole linker would affect the biological activity of the triazole-containing triterpene saponin analogs.

Herein, syntheses of previously unknown 1,2,3-triazole conjugates of lupane, ursane, and oleane triterpenoids with mono- and disaccharides based on Cu(I)-catalyzed 1,3-dipolar cycloaddition of azides to acetylenes (CuAAC) are reported. The CuAAC reaction has been widely employed in the last decade in medicinal and biological chemistry [7, 8]. Although triazole bridges are unknown in natural products, they possess several attractive properties such as high metabolic stability, water solubility, and the ability to form H-bonds with many enzymes.

C-2 propynyl derivatives of betulinic, ursolic, and oleanolic acids **1**–**3** were used to prepare triazolylglycopyranosides of triterpenoids **8a**–**d**, **9**, **10**, **11a**–**d**, **12**, and **13** (Scheme 1). These starting substrates with a terminal acetylene became available as a result of our development of α-alkylation by propargyl bromide of potassium enoxytriethylborates obtained from 3-ketotriterpenoids [9].

The sugar components, glycosylazides **4**–**7**, were prepared by reacting per-*O*-acetylated β-D-glucose, β-D-galactose, α-D-mannose, and β-D-lactose with trimethylsilylazide in the presence of $SnCl_4$. The spectral data of the obtained sugars agreed with the literature [10, 11].

The CuAAC between triterpenoids **1**–**3** and sugar azides **4**–**7** was carried out under conditions optimized by us earlier during studies of the conjugation of β-D-glucopyranose azide **4** with propynyl derivatives of betulinic (**1**) and ursolic acids (**2**) (Cu, $CuSO_4 \cdot 5H_2O$, *t*-BuOH, 40°C) [9] (Scheme 1).

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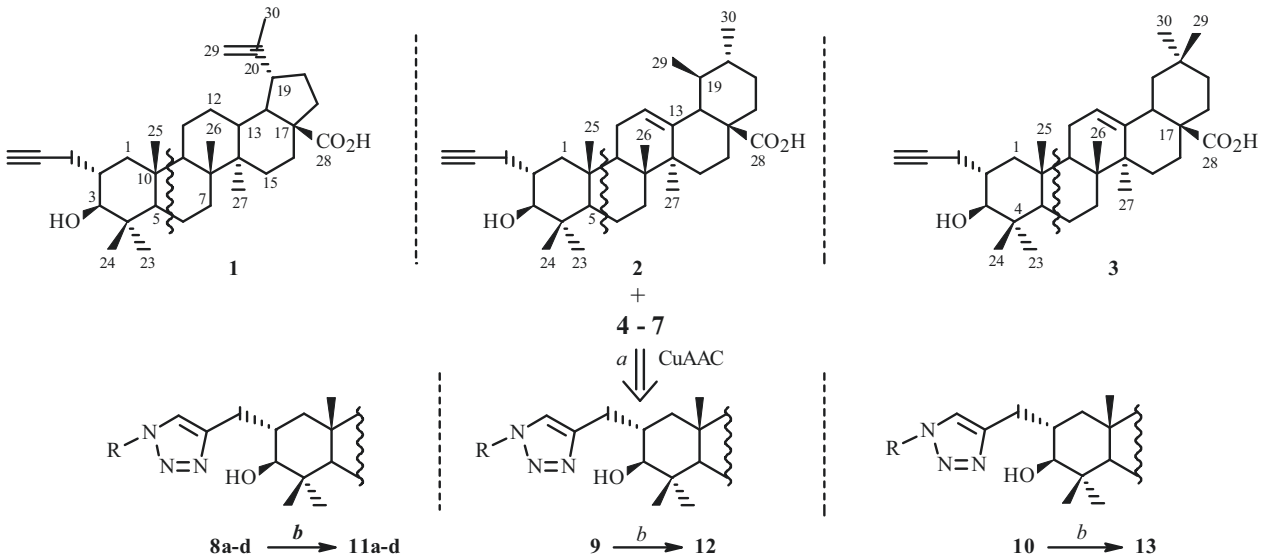
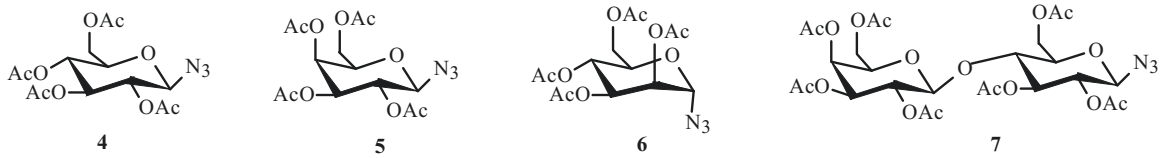


8a,9,10: R = per-*O*-Ac-β-D-Glc; **8b:** R = per-*O*-Ac-β-D-Gal; **8c:** R = per-*O*-Ac-α-D-Man; **8d:** R = per-*O*-Ac-Galβ(1→4)Glc; **11a,12,13:** R = β-D-Glc; **11b:** R = β-D-Gal; **11c:** R = α-D-Man; **11d:** R = Galβ(1→4)Glc

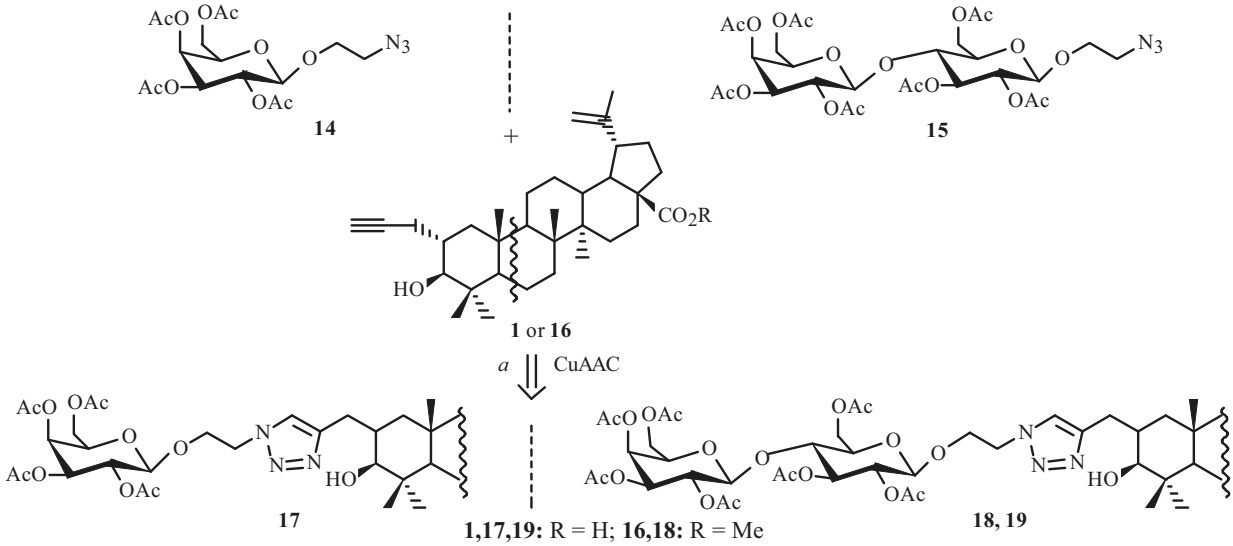
a. Cu powder, $CuSO_4 \cdot 5H_2O$, *t*-BuOH, 40°C; *b*. Et_3N, MeOH, H_2O, 20°C

Scheme 1



The type of triterpenoid aglycon (betulinic, ursolic, and oleanolic acids) was varied for future pharmacological studies of the structure–activity (cytotoxic) relationship of **8a**, **9**, and **10**. The triterpenoid aglycon (betulinic acid) in **8a**–**d** was linked through a 1,2,3-triazole ring to various sugars. The transformation terminated with de-*O*-acetylation of **8a**–**d**, **9**, and **10** using Et_3N in MeOH [12] to produce high yields of series of bioconjugates **11a**–**d**, **12**, and **13** with free hydroxyls in the sugars.

The 1,2,3-triazole ring and sugar in conjugates **8a**–**d**, **9**, **10**, **11a**–**d**, **12**, and **13** were linked through an *N*-glycoside bond. Compounds **17**–**19**, in which a spacer between the triazole ring and the sugar was bonded through an *O*-glycoside bond, were prepared in order to vary the sugar–triterpenoid bioconjugate structure. They were synthesized by reacting azidoethylglycosides of galactose (**14**) and lactose peracetates (**15**) with a propynyl derivative of **1** or methyl betulinate (**16**). Azides **14** and **15** were prepared using glycosylation of protected sugars by 2-bromoethanol in the presence of $BF_3 \cdot Et_2O$ in CH_2Cl_2 followed by reaction of the bromoethylglycosides with NaN_3 in DMF [13] (Scheme 2).



1,17,19: R = H; **16,18:** R = Me

a. Cu powder, $CuSO_4 \cdot 5H_2O$, *t*-BuOH, 40°C

Scheme 2

TABLE 1. ^{13}C NMR Spectral Data for **8a**–**d**, **9**, and **10** (δ, ppm)

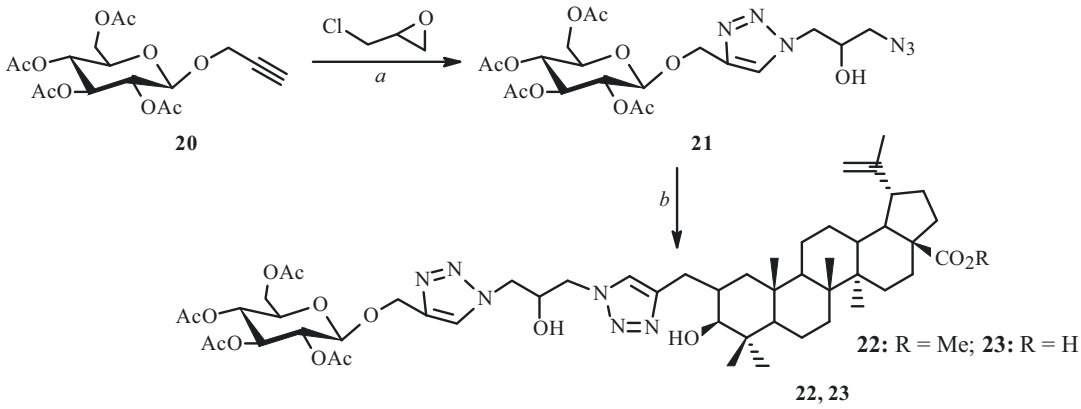
Atom or group	**8a**	**8b**	**8c**	**8d**	**9**	**10**
1	45.0	45.1	45.3	45.1	44.3	45.8
2	35.7	35.7	35.7	35.6	35.3	35.3
3	81.6	81.7	82.0	81.7	80.8	80.8
4	37.4	37.4	37.4	37.4	39.0	38.9
5	55.6	55.6	55.5	55.6	55.4	55.4
6	18.5	18.5	18.5	18.5	18.4	18.4
7	34.3	34.3	34.2	34.3	32.9	32.4
8	40.7	40.7	40.7	40.7	39.4	39.2
9	50.4	50.4	50.4	50.4	47.4	47.7
10	39.2	39.2	39.2	39.2	36.8	36.9
11	20.8	20.8	20.9	20.8	23.0	23.1
12	25.5	25.5	25.4	25.5	125.6	122.3
13	38.3	38.3	38.3	38.3	138.1	143.7
14	42.4	42.5	42.5	42.4	41.9	41.5
15	29.6	29.6	29.6	29.6	27.8	27.4
16	32.2	32.2	32.2	32.2	23.9	22.7
17	56.3	56.3	56.3	56.3	47.9	46.2
18	49.2	49.2	49.2	49.3	52.9	41.3
19	46.9	46.9	46.9	46.9	38.9	44.2
20	150.5	150.5	150.5	150.5	39.0	30.3
21	30.5	30.5	30.5	30.5	30.4	33.5
22	37.1	37.1	37.1	37.1	36.7	32.6
23	28.3	28.3	28.3	28.3	27.8	27.8
24	16.2	16.2	16.2	16.2	15.9	16.4
25	16.0	16.1	16.0	16.0	15.4	15.3
26	16.8	16.8	16.9	16.8	16.3	15.9
27	14.7	14.7	14.7	14.7	22.9	25.2
28	181.6	181.5	181.8	181.5	180.1	180.3
29	109.6	109.6	109.7	109.6	16.5	32.3
30	19.3	19.3	19.3	19.3	20.3	22.8
<u>CH</u>=C–N-	120.3	120.4	122.1	120.3	121.5	121.4
=C–<u>CH$_2$</u>	28.9	29.0	29.0	28.9	27.9	27.9
CH=<u>C</u>–N–	147.1	147.0	147.1	146.9	146.5	146.5
CO<u>CH$_3$</u>	20.7, 20.6	20.7, 20.6	20.7, 20.6	20.7, 20.6	19.3, 19.2	19.3, 19.2
	20.5, 20.1	20.5, 20.2	20.5, 20.3	20.5, 20.3	19.1, 18.9	19.1, 18.9
$COCH_3$	170.5, 169.9	170.4, 170.0	170.5, 170.0	170.4, 170.3	170.8, 170.1	170.8, 170.1
	169.4, 168.9	169.8, 169.1	169.7, 169.4	170.2, 170.1	169.8, 168.6	169.8, 168.6
				169.5, 169.1		
1′–6′	85.7, 75.1	86.2, 74.0	83.4, 72.1	85.5, 75.9	85.4, 74.6	85.4, 74.5
1″–6″	72.6, 70.3	70.8, 67.9	68.9, 68.2	75.7, 72.5	72.6, 70.8	72.5, 70.7
	67.8, 61.6	66.9, 61.2	66.2, 61.5	70.9, 61.8	67.9, 61.6	67.9, 61.6
				101.1, 70.8		
				70.6, 69.1		
				66.6, 60.8		

A bis-triazole linker was constructed in the glycosylated triterpenoids using our previously developed methodology for three-component cycloaddition of NaN_3 and epichlorohydrin to propargylglycosides, which occurs with regioselective opening of the oxirane ring of epichlorohydrin under CuAAC conditions [14]. 2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranose *β*-propargylglycoside (**20**) was chosen as the starting sugar substrate. It was synthesized by reacting commercially available *β*-D-glucopyranose pentaacetate with propargyl alcohol [15]. The one-pot condensation of **20** and excesses of epichlorohydrin (2.0 eq) and NaN_3 (4.0 eq) in the presence of $CuSO_4 \cdot 5H_2O$ and NaAsc in H_2O at room temperature gave triazolylazide alcohol **21** in acceptable (56%) yield. The last underwent Cu(I)-catalyzed conjugation with triterpenoids **1** and **16** (Scheme 3).

TABLE 2. ^{13}C NMR Spectral Data for **11b**–**d**, **13**, and **17**–**19** (δ, ppm)

Atom or group	**11b**	**11c**	**11d**	**13**	**17**	**18**	**19**
1	44.9	44.9	46.4	46.0	45.2	45.3	46.3
2	35.9	35.9	37.4	35.6	35.7	35.6	37.4
3	81.5	81.5	83.0	81.6	81.7	81.7	83.1
4	37.0	37.0	38.5	38.9	38.3	37.4	38.5
5	55.6	55.6	57.1	55.5	55.6	55.6	57.1
6	18.3	18.3	19.8	18.4	18.5	18.5	19.8
7	34.2	34.2	35.7	32.5	34.3	34.2	35.7
8	40.6	40.6	42.1	39.2	40.7	40.7	42.1
9	50.5	50.6	52.1	47.8	50.4	50.4	52.0
10	39.0	39.0	40.5	36.9	39.2	39.1	40.5
11	20.7	20.7	22.2	23.1	20.8	20.8	22.3
12	25.5	25.5	27.0	122.1	25.5	25.5	27.0
13	38.2	38.2	39.8	143.9	38.3	38.2	39.7
14	42.2	42.3	43.7	41.6	42.4	42.4	43.7
15	29.4	29.5	30.9	27.5	29.6	29.6	31.0
16	32.0	32.3	33.5	22.7	32.2	32.1	33.7
17	56.1	56.2	57.6	46.3	56.3	56.5	57.8
18	49.0	49.1	50.6	41.4	49.3	49.4	50.6
19	47.1	47.2	48.6	44.6	46.9	47.0	49.2
20	150.6	150.8	152.1	30.3	150.5	150.5	152.3
21	30.3	30.4	31.8	33.6	30.5	30.5	31.9
22	36.8	37.0	38.3	32.6	37.1	36.9	38.5
23	27.7	27.7	29.2	27.8	28.4	28.3	29.2
24	15.6	15.7	17.1	16.5	16.2	16.2	17.2
25	15.3	15.4	16.8	15.3	16.1	15.9	16.9
26	16.1	16.1	17.6	15.9	16.9	16.8	17.7
27	13.8	13.8	15.3	25.1	14.7	14.7	15.4
28	178.8	–	180.4	181.4	181.6	176.6	181.6
29	108.8	108.7	110.3	32.3	109.7	109.6	110.3
30	18.2	18.2	19.7	22.7	19.3	19.3	19.8
CH=C–N–	121.5	121.7	123.7	122.1	123.3	123.0	124.8
=C–CH_2	28.4	28.4	29.9	28.3	28.4	29.2	29.9
CH=C–N–	146.3	146.3	–	146.1	146.1	146.1	147.6
CH_2–O	–	–	–	–	67.8	67.9	69.0
CH_2–N	–	–	–	–	50.0	50.0	51.3
$COCH_3$	–	–	–	–	20.7, 20.6	20.7, 20.6	21.0, 20.9
					20.5, 20.4	20.5, 20.3	20.8, 20.7
$COCH_3$	–	–	–	–	170.4, 170.2	170.3, 170.1	172.4, 172.0
					170.0, 169.6	170.0, 169.7	171.7, 171.5
						169.6, 169.0	171.2, 171.1
CO_2Me	–	–	–	–	–	51.2	–
1′–6′	88.7, 78.6	88.6, 78.4	89.3, 79.8	88.0, 79.7	100.9, 70.9	100.3, 76.1	100.2, 77.8
1″–6″	74.0, 69.9	74.0, 69.9	79.7, 77.3	77.2, 72.6	70.6, 68.5	72.8, 72.4	74.3, 74.2
	69.0, 61.1	69.1, 61.1	77.1, 62.7	69.5, 61.0	66.9, 61.2	71.4, 61.7	72.9, 63.6
			105.2, 74.9			101.0, 70.9	100.6, 72.5
			73.7, 72.7			70.7, 69.1	71.9, 70.8
			70.5, 61.7			66.6, 60.8	68.7, 62.4

Conjugation between alkyne **16** and triazolylazide **21** in the presence of Cu powder and $CuSO_4 \cdot 5H_2O$ in *t*-BuOH at 40°C gave bioconjugate **22** in yields <20%. An attempt to produce **22** using CuI in the presence of diisopropylethylamine in refluxing THF was unsuccessful, probably because of the low reactivity of triazolylazide **21**. Target product **22** was obtained in 62% yield via CuI-catalyzed reaction of **21** with **16** in *t*-BuOH under Ar for 23 h at 70°C. Under these conditions, the reaction afforded conjugate **23** in 53% yield. Conjugates **22** and **23** were chromatographically inseparable mixtures (1:1, PMR data) of the *R*/*S*-diastereomers relative to the CH–OH C atom in the bis-triazole linker.



a. NaN_3, H_2O, $CuSO_4 \cdot 5H_2O$, NaAsc; *b*. **1** or **16**, CuI, *t*-BuOH, 70°C, 23 h

Scheme 3

The structures of all synthesized compounds were confirmed by 1D (PMR, ^{13}C NMR, APT) and 2D homo- (COSY, NOESY) and heteronuclear experiments (HSQC, HMBC). Chemical shifts of terpene skeleton atoms were determined by a comparison with the literature [9]. The appearance in PMR spectra of **8a**–**d**, **9**, **10**, **11a**–**d**, **12**, **13**, and **17**–**19** of characteristic resonances for C<u>H</u>=C–N at δ 7.33–8.04 was consistent with formation of triazole rings. ^{13}C NMR spectra showed resonances of [1,5]-triazole C atoms <u>C</u>H=C–N and CH=<u>C</u>–N at 120.3–124.8 and 146.3–147.9 ppm, respectively (Tables 1 and 2).

Strong absorption in the IR spectrum of **21** at 2106 cm^{-1} was consistent with an azide. PMR spectra exhibited a resonance for the triazole-ring proton at δ 7.69. A comparison of PMR and ^{13}C NMR spectra of **22** and **23** with those of **21** confirmed that they had formed. Thus, the protons of both triazole rings resonated as four singlets at δ 7.48, 7.50, 7.75, and 7.76 in the PMR spectrum of the diastereomeric mixture of **22**. C atoms of triazole rings bound to sugars <u>C</u>H=C–N and CH=<u>C</u>–N resonated at δ 125.0 and 143.8. Resonances of [1,5]-triazole C atoms of the second triazole ring were found at δ 123.9, 123.8 and 146.3, 146.4. Anomeric sugar proton H-1′ appeared as a doublet at δ 4.71 with SSCC J = 8.0 Hz, typical for a *β*-glycoside bond.

Cytotoxic activity of the synthesized glycoside triterpenoid derivatives was studied using standard procedures at the National Cancer Institute (NCI, USA) on panels consisting of 60 human tumor cell lines (leukemia, melanoma and cancer of the lung, colon, kidneys, ovaries, breasts, prostate, and CNS) (http://dtp.cancer.gov/btp/ivclsp.html). All compounds at the single concentration 10^{-5} M exhibited weak cytotoxic activity that did not meet selection criteria for second stage testing at five different doses.

Thus, Cu(I)-catalyzed 1,3-dipolar cycloaddition of alkynes and azides synthesized series of new C-2 glycoconjugates of lupane-, ursane-, and oleane-type triterpenoids in which the sugar moiety and triterpene core are linked through biologically active mono- or bis-1*H*-1,2,3-triazole rings. Considering the broad spectra of biological activities found for natural triterpene saponins, we plan further biological studies of this new family of glycosylated triterpene-acid derivatives.

EXPERIMENTAL

IR spectra were taken from thin layers or $CHCl_3$ solutions on a Bruker Vertex 70 V spectrometer. PMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_3OD with TMS internal standard on a Bruker Avance-500 (operating frequency 500.13 MHz for ^1H and 125.78 MHz for ^{13}C) or Bruker Avance-400 instrument (operating frequency 400.13 and 100.62 MHz, respectively). MALDI TOF mass spectra were recorded in positive-ion mode using 2,5-dihydroxybenzoic and *α*-cyano-4-hydroxycinnamic acids as matrices on a Bruker Autoflex III spectrometer. Optical rotation was determined on a PerkinElmer-141 polarimeter where $[\alpha]_D$ is the specific rotation [deg·mL·(g·dm)$^{-1}$]; *c*, solution concentration [g·(100 mL)$^{-1}$]. Elemental analyses were measured on a Carlo Erba 1106 analyzer. TLC used Sorbfil plates (Sorbpolimer, Krasnodar, Russia) and hexane–EtOAc or $CHCl_3$–MeOH (4:1) with anisaldehyde detector. Column chromatography was performed over silica gel L (50–160 μm, KSKG grade). $SnCl_4$ (1 M in CH_2Cl_2), CH_3COCl, $TMSiN_3$, Et_3N, $BF_3 \cdot Et_2O$, 2-bromoethanol, $CeCl_3 \cdot 7H_2O$, $NaBH_4$, LiI, DMF, *t*-BuOH, Cu powder, NaN_3, sodium ascorbate, epichlorohydrin, betulinic acid, ursolic acid, oleanolic acid, $KN(SiMe_3)_2$ (1 M in THF), BEt_3 (95%), propargyl bromide, and propargyl alcohol were purchased (Aldrich). Solvents were prepared as usual. All reactions were conducted under Ar. Triterpenoids **1**–**3** and **16** were prepared as before [9]. Spectral data for **11a** and

12 agreed with the literature [9]. Elemental analyses of all new compounds agreed with those calculated. Tables 1 and 2 present ^{13}C NMR spectral data for **8a**–**d**, **9**, **10**, **11b**–**d**, **13**, and **17**–**19**.

Reaction of 1–3 and 16 with Glycosylazides 4–7, 14, and 15. General Method. A solution of **1**, **2**, **3**, or **16** (0.4 mmol) in *t*-BuOH (6 mL) was treated in turn with glycosylazide **4**–**7**, **14**, or **15** (0.5 mmol), Cu powder (0.014 g, 0.22 mmol), and $CuSO_4 \cdot 5H_2O$ solution (0.08 mL, 1 M, 0.08 mmol); heated for 20–24 h at 40°C (TLC monitoring); cooled; filtered over a column with a thin layer of silica gel to remove Cu powder; poured into H_2O; and extracted with CH_2Cl_2 (30 mL). The organic layer was washed with H_2O (30 mL) and dried ($MgSO_4$). The products were purified by column chromatography over silica gel [*n*-hexane–EtOAc (1:1) or $CHCl_3$–MeOH eluent (4:1)] to afford **8a**–**d**, **9**, **10**, **17**, **18**, or **19**.

2α-Methylene-[1*N*(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranos-1-yl)-1*H*-1,2,3-triazol-4-yl]-3β-hydroxylup-20(29)-en-28-oic Acid (8a). $C_{47}H_{69}N_3O_{12}$. Yield 89%, mp 164–168°C, $[\alpha]_D^{22}$ –11° (*c* 1.2, $CHCl_3$). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1757 (C=O), 3471 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.78, 0.80, 0.90, 0.93, 0.96 (3H each, s, CH_3-23–27), 1.67 (3H, s, CH_3-30), 0.62–2.27 (23H, m, CH, CH_2 in pentacyclic skeleton), 1.84, 2.03, 2.07, 2.08 (3H each, s, $CO\underline{CH_3}$), 2.68 (1H, dd, J = 14.0, 7.0, H_a-CH_2), 2.78 (1H, d, J = 10.5, H-3), 2.97–3.02 (2H, m, H-19, H_b-CH_2), 3.99–4.03 (1H, m, H-5′), 4.15 (1H, d, J = 12.5, H_a-6′), 4.31 (1H, dd, J = 12.5, 5.0, H_b-6′), 4.59, 4.71 (1H each, br.s, H-29), 5.24 (1H, t, J = 9.5, H-4′), 5.40–5.46 (2H, m, H-3′, 2′), 5.83 (1H, d, J = 9.0, H-1′), 7.59 (1H, s, $\underline{CH}$=C–N). MS *m/z* 890.5 $[M + Na]^+$ (calcd for $C_{47}H_{69}N_3O_{12}$, 867.5).

2α-Methylene-[1*N*(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranos-1-yl)-1*H*-1,2,3-triazol-4-yl]-3β-hydroxylup-20(29)-en-28-oic Acid (8b). $C_{47}H_{69}N_3O_{12}$. Yield 92%, mp 136–138°C, $[\alpha]_D^{18}$ –2° (*c* 0.9, $CHCl_3$). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1756 (C=O), 3474 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.80, 0.82, 0.92, 0.95, 0.97 (3H each, s, CH_3-23–27), 1.68 (3H, s, CH_3-30), 0.66–2.28 (23H, m, CH, CH_2 in pentacyclic skeleton), 1.87, 2.02, 2.05, 2.23 (3H each, s, $CO\underline{CH_3}$), 2.73 (1H, dd, J = 14.0, 7.0, H_a-CH_2), 2.80 (1H, d, J = 11.0, H-3), 2.98–3.03 (2H, m, H-19, H_b-CH_2), 4.12–4.24 (3H, m, H-5′, H_{ab}-6′), 4.59, 4.72 (1H each, br.s, H-29), 5.26 (1H, dd, J = 11.0, 3.5, H-3′), 5.53–5.57 (2H, m, H-2′, 4′), 5.83 (1H, d, J = 10.0, H-1′), 7.63 (1H, s, $\underline{CH}$=C–N). MS *m/z* 890.5 $[M+Na]^+$ (calcd for $C_{47}H_{69}N_3O_{12}$, 867.5).

2α-Methylene-[1*N*(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranos-1-yl)-1*H*-1,2,3-triazol-4-yl]-3β-hydroxylup-20(29)-en-28-oic Acid (8c). $C_{47}H_{69}N_3O_{12}$. Yield 87%, mp 156–158°C, $[\alpha]_D^{18}$ +18.5° (*c* 0.8, $CHCl_3$). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1754 (C=O), 3448 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.80, 0.83, 0.91, 0.96, 0.98 (3H each, s, CH_3-23–27), 1.68 (3H, s, H-30), 2.05, 2.07, 2.09, 2.17 (3H each, s, $CO\underline{CH_3}$), 0.64–2.26 (23H, m, CH, CH_2 in pentacyclic skeleton), 2.69–2.73 (1H, m, H_a-CH_2), 2.84 (1H, d, J = 11.0, H-3), 3.00–3.06 (2H, m, H-19, H_b-CH_2), 3.87–3.89 (1H, m, H-5′), 4.05 (1H, d, J = 12.5, H_a-6′), 4.38 (1H, dd, J = 12.5, 5.5, H_b-6′), 4.59, 4.72 (1H each, br.s, H-29), 5.36 (1H, t, J = 10.0, H-4′), 5.90–5.92 (2H, m, H-2′, 3′), 5.98 (1H, d, J = 11.5, H-1′), 7.52 (1H, s, $\underline{CH}$=C–N). MS *m/z* 890.3 $[M + Na]^+$ (calcd for $C_{47}H_{69}N_3O_{12}$, 867.5).

2α-Methylene-[1*N*(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-β-D-glucopyranos-1-yl)-1*H*-1,2,3-triazol-4-yl]-3β-hydroxylup-20(29)-en-28-oic Acid (8d). $C_{59}H_{85}N_3O_{20}$. Yield 86%, mp 166–168°C, $[\alpha]_D^{21}$ –14.4° (*c* 0.7, CH_3OH). IR spectrum (CH_3OH, ν, cm^{-1}): 1753 (C=O), 3444 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.79, 0.83, 0.89, 0.93, 0.95 (3H each, s, CH_3-23–27), 1.67 (3H, s, H-30), 1.84, 1.97, 2.05, 2.06, 2.08, 2.10, 2.16 (3H each, s, $CO\underline{CH_3}$), 0.64–2.26 (23H, m, CH, CH_2 in pentacyclic skeleton), 2.69–2.78 (1H, m, H_a-CH_2), 2.76 (1H, d, J = 10.0, H-3), 2.97–2.99 (2H, m, H-19, H_b-CH_2), 3.91–3.99, 4.11–4.17 (6H, 2 m, H_a-6′, H_{ab}-6″, H-4′, 5′, 5″), 4.49 (1H, d, J = 10.0, H_b-6′), 4.53 (1H, d, J = 8.0, H-1″), 4.58, 4.71 (1H each, br.s, H-29), 4.98 (1H, dd, J = 10.5, 3.5, H-3″), 5.13 (1H, t, J = 8.0, H-2′), 5.37–5.43 (3H, m, H-2″, 3′, 4″), 5.80 (1H, d, J = 10.0, H-1′), 7.50 (1H, s, $\underline{CH}$=C–N). MS *m/z* 1178.7 $[M + Na]^+$ (calcd for $C_{59}H_{85}N_3O_{20}$, 1155.6).

2α-Methylene-[1*N*(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranos-1-yl)-1*H*-1,2,3-triazol-4-yl]-3β-hydroxyurs-12-en-28-oic Acid (9). $C_{47}H_{69}N_3O_{12}$. Yield 89%, mp 152–154°C, $[\alpha]_D^{22}$ +10° (*c* 1.1, $CHCl_3$). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1757 (C=O), 3474 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.88 (3H, d, J = 6.5, H-29), 0.94 (3H, s, H-30), 0.84, 0.85, 0.98, 1.04, 1.10 (3H each, s, CH_3-23–27), 0.60–2.26 (22H, m, CH, CH_2 in pentacyclic skeleton), 1.85, 2.03, 2.07, 2.08 (3H each, s, $CO\underline{CH_3}$), 2.62 (1H, dd, J = 13.5, 8.5, H_a-CH_2), 2.86 (1H, d, J = 10.5, H-3), 3.10 (1H, d, J = 13.5, H_b-CH_2), 4.20 (1H, d, J = 12.5, H_a-6′), 4.25–4.28 (1H, m, H-5′), 4.36 (1H, dd, J = 12.5, 5.0, H_b-6′), 5.22 (1H, s, H-12), 5.28–5.34 (1H, m, H-2′), 5.53–5.59 (2H, m, H-4′, 3′), 6.11 (1H, d, J = 8.5, H-1′), 8.04 (1H, s, $\underline{CH}$=C–N). MS *m/z* 890.4 $[M + Na]^+$ (calcd for $C_{47}H_{69}N_3O_{12}$, 867.5).

2α-Methylene-[1*N*(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranos-1-yl)-1*H*-1,2,3-triazol-4-yl]-3β-hydroxyolean-12-en-28-oic Acid (10). $C_{47}H_{69}N_3O_{12}$. Yield 88%, mp 168–170°C, $[\alpha]_D^{21}$ +17.9° (*c* 0.9, $CHCl_3$). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1757 (C=O), 2946 (C=C), 3476 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.81, 0.85, 0.91, 0.92, 0.96, 1.03, 1.14 (3H each, s, CH_3-23–27, 29, 30), 1.22–2.02 (21H, m, CH, CH_2 in pentacyclic skeleton), 1.85, 2.03, 2.06, 2.08 (3H each, s, $CO\underline{CH_3}$), 2.62 (1H, dd, J = 14.0, 8.5, H_a-CH_2), 2.83–2.87 (2H, m, H-3, 18), 3.11 (1H, d, J = 14.0, H_b-CH_2), 4.19–4.28 (2H, m, H-5′, H_a-6′), 4.36

(1H, dd, J = 13.0, 5.0, H_b-6′), 5.23 (1H, s, H-12), 5.30 (1H, t, J = 9.5, H-4′), 5.53–5.59 (2H, m, H-2′, 3′), 6.12 (1H, d, J = 8.5, H-1′), 8.02 (1H, s, CH=C–N). MS *m/z* 890.6 $[M + Na]^+$ (calcd for $C_{47}H_{69}N_3O_{12}$, 867.5).

2α-Methylene-[1*N*(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranos-1-yl)-ethylene-1*H*-1,2,3-triazol-4-yl]-3β-hydroxylup-20(29)-en-28-oic Acid (17). $C_{49}H_{73}N_3O_{13}$. Yield 85%, mp 152–154°C, $[\alpha]_D^{18}$ –17° (*c* 0.8, $CHCl_3$). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1752 (C=O), 3467 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.80, 0.83, 0.91, 0.94, 0.97 (3H each, s, CH_3-23–27), 1.68 (3H, s, CH_3-30), 0.59–2.26 (23H, m, CH, CH_2 in pentacyclic skeleton), 1.94, 1.98, 2.05, 2.17 (3H each, s, $CO\underline{CH_3}$), 2.79–2.91 (3H, m, H-3, CH_2), 3.00–3.04 (1H, m, H-19), 3.88–3.93, 4.11–4.17, 4.25–4.26, 4.51–4.53, 4.57–4.63 (7H, 5 m, H-5′, H_{ab}-6′, CH_2-O, CH_2-N), 4.44 (1H, d, J = 10.0, H-1′), 4.59, 4.72 (1H each, br.s, H-29), 4.98 (1H, dd, J = 10.0, 3.5, H-3′), 5.17–5.21 (1H, m, H-2′), 5.39 (1H, s, H-4′), 7.39 (1H, s, CH=C–N). MS *m/z* 934.3 $[M + Na]^+$ (calcd for $C_{49}H_{73}N_3O_{13}$, 911.5).

Methyl 2α-Methylene-[1*N*(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-β-D-glucopyranos-1-yl)-ethylene-1*H*-1,2,3-triazol-4-yl]-3β-hydroxylup-20(29)-en-28-oate (18). $C_{62}H_{91}N_3O_{21}$. Yield 89%, mp 142–144°C, $[\alpha]_D^{21}$ –18.3° (*c* 0.9, $CHCl_3$). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1753 (C=O). ^1H NMR spectrum (δ, ppm, J/Hz): 0.78, 0.80, 0.87, 0.91, 0.95 (3H each, s, CH_3-23–27), 1.66 (3H, s, H-30), 1.93, 1.94, 2.02, 2.03, 2.04, 2.10, 2.13 (3H each, s, $CO\underline{CH_3}$), 0.57–2.26 (23H, m, CH, CH_2 in pentacyclic skeleton), 2.73 (1H, dd, J = 15.0, 7.0, H_a-CH_2), 2.79 (1H, d, J = 10.0, H-3), 2.83–2.87 (1H, m, H_b-CH_2), 2.95–2.99 (1H, m, H-19), 3.57–3.60 (1H, m, H-5′), 3.64 (3H, s, OCH_3), 3.75–3.78, 3.83–3.89, 4.04–4.18 (7H, 3 m, H_a-6′, H_{ab}-6″, H-4′, 5″, CH_2-O), 4.42–4.50, 4.54–4.56 (5H, 2m, H_b-6′, H-1″, 1′, CH_2-N), 4.57, 4.70 (1H each, br.s, H-29), 4.87 (1H, t, J = 8.0, H-2′), 4.95 (1H, dd, J = 10.5, 3.5, H-3″), 5.08 (1H, dd, J = 10.0, 8.0, H-2″), 5.15 (1H, t, J = 10.0, H-3′), 5.33 (1H, d, J = 3.0, H-4″), 7.33 (1H, s, CH=C–N). MS *m/z* 1236.9 $[M + Na]^+$ (calcd for $C_{62}H_{91}N_3O_{21}$, 1213.6).

2α-Methylene-[1*N*(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-β-D-glucopyranos-1-yl)-ethylene-1*H*-1,2,3-triazol-4-yl]-3β-hydroxylup-20(29)-en-28-oic Acid (19). $C_{61}H_{89}N_3O_{21}$. Yield 90%, mp 168–170°C, $[\alpha]_D^{21}$ –20.5° (*c* 0.7, CH_3OH). IR spectrum (CH_3OH, ν, cm^{-1}): 1753 (C=O), 3469 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.79, 0.82, 0.83, 0.97, 1.00 (3H each, s, CH_3-23–27), 1.70 (3H, s, H-30), 1.95, 1.97, 2.05, 2.06, 2.07, 2.13, 2.15 (3H each, s, $CO\underline{CH_3}$), 0.60–2.26 (23H, m, CH, CH_2 in pentacyclic skeleton), 2.46–2.52 (1H, m, H_a-CH_2), 2.83 (1H, d, J = 10.0, H-3), 3.03–3.10, 3.17–3.19 (2H, 2m, H_b-CH_2, H-19), 3.76–3.79, 3.83–3.87, 3.98–4.02, 4.10–4.17 (8H, 4 m, H_a-6′, H_{ab}-6″, H-4′, 5″, CH_2-O, H-5′), 4.54–4.56, 4.66–4.68 (5H, 2m, H_b-6′, H-1″, 1′, CH_2-N), 4.59, 4.72 (1H each, br.s, H-29), 4.83 (1H, t, J = 8.0, H-2′), 5.03 (1H, dd, J = 10.5, 3.5, H-3″), 5.13–5.21 (2H, m, H-2″, 3′), 5.38 (1H, d, J = 3.0, H-4″), 7.69 (1H, s, CH=C–N). MS *m/z* 1222.6 $[M + Na]^+$ (calcd for $C_{61}H_{89}N_3O_{21}$, 1199.6).

Synthesis of 11a–d, 12, and 13. General Method. A solution of **8a**–**d**, **9**, or **10** (0.1 mmol) in MeOH (2 mL) and H_2O (0.2 mL) was treated with Et_3N (0.5 mmol), stirred for 3–4 h at room temperature (TLC monitoring), and evaporated. The products were purified by column chromatography over silica gel [*n*-hexane–EtOAc (1:1) or $CHCl_3$–MeOH eluent (4:1)] to afford **11a**–**d**, **12**, or **13**. PMR and ^{13}C NMR spectra and physicochemical constants of **11a** and **12** were published before [9].

2α-Methylene-[1*N*(β-D-galactopyranos-1-yl)-1*H*-1,2,3-triazol-4-yl]-3β-hydroxylup-20(29)-en-28-oic Acid (11b). $C_{39}H_{61}N_3O_8$. Yield 90%, mp 220–222°C, $[\alpha]_D^{18}$ –24° (*c* 0.8, CH_3OH). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1697 (C=O), 3437 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.82, 0.83, 0.96, 0.99, 1.01 (3H each, s, CH_3-23–27), 1.71 (3H, s, CH_3-30), 0.63–2.32 (23H, m, CH, CH_2 in pentacyclic skeleton), 2.54 (1H, dd, J = 14.5, 9.0, H_a-CH_2), 2.83 (1H, d, J = 11.0, H-3), 3.00–3.05 (1H, m, H-19), 3.18 (1H, d, J = 14.5, H_b-CH_2), 3.70–3.89 (4H, m, H-5′, H_{ab}-6′, H-3′), 4.00 (1H, br.s, H-4′), 4.19 (1H, t, J = 9.0, H-2′), 4.61, 4.72 (1H each, br.s, H-29), 5.55 (1H, d, J = 9.5, H-1′), 7.97 (1H, s, CH=C–N). MS *m/z* 722.4 $[M + Na]^+$ (calcd for $C_{39}H_{61}N_3O_8$, 699.5).

2α-Methylene-[1*N*(α-D-mannopyranos-1-yl)-1*H*-1,2,3-triazol-4-yl]-3β-hydroxylup-20(29)-en-28-oic Acid (11c). $C_{39}H_{61}N_3O_8$. Yield 70%, mp 256–258°C, $[\alpha]_D^{21}$ –18° (*c* 0.7, CH_3OH). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1725 (C=O), 3442 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.82, 0.83, 0.97, 0.99, 1.00 (3H each, s, CH_3-23–27), 1.70 (3H, s, CH_3-30), 0.63–2.36 (23H, m, CH, CH_2 in pentacyclic skeleton), 2.53–2.57 (1H, m, H_a-CH_2), 2.84 (1H, d, J = 11.0, H-3), 3.07–3.09 (1H, m, H-19), 3.18 (1H, d, J = 14.0, H_b-CH_2), 3.73–3.87 (4H, m, H-5′, H_{ab}-6′, H-3′), 4.03 (1H, br.s, H-4′), 4.19 (1H, t, J = 9.0, H-2′), 4.59, 4.70 (1H each, br.s, H-29), 5.56 (1H, d, J = 9.0, H-1′), 7.99 (1H, s, CH=C–N). MS *m/z* 722.4 $[M + Na]^+$ (calcd for $C_{39}H_{61}N_3O_8$, 699.5).

2α-Methylene-[1*N*(β-D-galactopyranosyl)-(1→4)-(β-D-glucopyranos-1-yl)-1*H*-1,2,3-triazol-4-yl]-3β-hydroxylup-20(29)-en-28-oic Acid (11d). $C_{45}H_{71}N_3O_{12}$. Yield 84%, mp 236–238°C, $[\alpha]_D^{21}$ –22° (*c* 0.8, CH_3OH). IR spectrum (CH_3OH, ν, cm^{-1}): 1683 (C=O), 3452 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.82, 0.83, 0.96, 0.99, 1.00 (3H each, s, CH_3-23–27), 1.71 (3H, s, H-30), 0.62–2.32 (23H, m, CH, CH_2 in pentacyclic skeleton), 2.51–2.56 (1H, m, H_a-CH_2), 2.82 (1H, d, J = 10.0, H-3), 3.00–3.05 (1H, m, H-19), 3.16–3.20 (1H, m, H_b-CH_2), 3.50–3.66, 3.73–3.95, 4.00–4.04 (12H, 3m, CH-OH,

CH_2OH in disaccharide), 4.44 (1H, d, J = 8.0, H-1″), 4.61, 4.72 (1H each, br.s, H-29), 5.62 (1H, d, J = 10.0, H-1′), 7.94 (1H, s, CH=C-N). MS *m/z* 884.3 $[M + Na]^+$ (calcd for $C_{45}H_{71}N_3O_{12}$, 861.5).

2α-Methylene-[1*N*(β-D-glucopyranos-1-yl)-1*H*-1,2,3-triazol-4-yl]-3β-hydroxyolean-12-en-28-oic Acid (13). $C_{39}H_{61}N_3O_8$. Yield 93%, mp 220–222°C, $[\alpha]_D^{18}$ –1° (*c* 0.8, CH_3OH). IR spectrum (CH_3OH, ν, cm^{-1}): 1695 (C=O), 2944 (C=C), 3383 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.78, 0.81, 0.88, 0.89, 0.92, 0.98, 1.13 (3H each, s, CH_3-23–27, 29, 30), 0.64–1.99 (21H, m, CH, CH_2 in pentacyclic skeleton), 2.51 (1H, dd, J = 14.5, 9, H_a-CH_2), 2.81–2.83 (2H, m, H-3, 18), 3.14 (1H, d, J = 14.5, H_b-CH_2), 3.47–3.58 (3H, m, H-3′, 4′, 5′), 3.69–3.72 (1H, m, H_a-6′), 3.86–3.91 (2H, m, H-2′, H_b-6′), 5.19 (1H, s, H-12), 5.55 (1H, d, J = 9.0, H-1′), 7.91 (1H, s, CH=C-N). MS *m/z* 722.5 $[M + Na]^+$ (calcd for $C_{39}H_{61}N_3O_8$, 699.5).

Reactions of Triterpenoids 1 and 16 with Triazolylazide 21. General Method. A solution of triterpenoid **1** or **16** (0.2 mmol) in *t*-BuOH (3 mL) was treated in turn with triazolylazide **21** (0.3 mmol) and CuI (0.008 g, 0.04 mmol), stirred for 23 h at 70°C (TLC monitoring), cooled, treated with H_2O (6 mL), and extracted (4 × 10 mL) with EtOAc. The organic layer was washed with H_2O (40 mL) and dried ($MgSO_4$). The products were purified by column chromatography over silica gel ($CHCl_3$–MeOH eluent, 15:1) to afford **22** or **23**.

3-Azido-[1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranos-1-yl)-methylene-1*H*-1,2,3-triazol-4-yl]propan-2-ol (21) was prepared by the literature method [14]. $C_{20}H_{28}N_6O_{11}$. Yield 56%, amorphous compound, $[\alpha]_D^{25}$ –18.6° (*c* 0.6, $CHCl_3$). IR spectrum ($CHCl_3$, ν, cm^{-1}): 2106 (N_3). ^1H NMR spectrum (δ, ppm, J/Hz): 1.98, 1.99, 2.02, 2.08 (3H each, s, $CO\underline{CH_3}$), 3.54–3.61 (2H, m, CH_2-N_3), 3.72–3.75 (1H, m, H-5), 4.15 (1H, d, J = 12.5, H_a-6), 4.26 (1H, dd, J = 12.5, 4.0, H_b-6), 4.28–4.33 (1H, m, CH-OH), 4.60–4.65 (2H, m, CH_2-O), 4.68 (1H, d, J = 8.0, H-1), 4.78 (1H, dd, J = 13.0, = 4.0, H_a-CH_2N), 4.88 (1H, d, J = 13.0, H_b-CH_2N), 4.95–4.99 (1H, m, H-2), 5.08 (1H, t, J = 10.0, H-4), 5.20 (1H, t, J =10.0, H-3), 7.69 (1H, s, CH=C-N). ^{13}C NMR spectrum (δ, ppm, J/Hz): 20.8 ($CO\underline{CH_3}$), 45.9 (CH_2-N_3), 53.1 (CH_2-O), 61.8 (C-6), 62.9 (CH_2-N), 68.3 (C-4), 69.9 (CH-OH), 71.3 (C-2), 71.9 (C-5), 72.7 (C-3), 100.0 (C-1), 124.6, 124.7 (CH=C-N), 144.0 (CH=C-N), 169.4, 169.5, 170.2, 170.8 ($\underline{C}OCH_3$). MS *m/z* 567.1 $[M + K]^+$ (calcd for $C_{20}H_{28}N_6O_{11}$, 528.2).

Methyl 2α-Methylene-{1*N*-1*H*-1,2,3-triazol-4-yl-[3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranos-1-yl)-methylene-1*H*-1,2,3-triazol-4-ylpropan-2-ol]}-3β-hydroxylup-20(29)-en-28-oate (22). $C_{54}H_{80}N_6O_{14}$. Yield 62%, mp 128–130°C, $[\alpha]_D^{25}$ –19.1° (*c* 0.7, $CHCl_3$). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1757 (C=O), 3444 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.79, 0.81, 0.90, 0.94, 0.96 (3H each, s, CH_3-23–27), 1.68 (3H, s, CH_3-30), 0.59–2.25 (23H, m, CH, CH_2 in pentacyclic skeleton), 2.01, 2.04, 2.09, 2.10 (3H each, s, $CO\underline{CH_3}$), 2.59–2.65 (1H, m, H_a-CH_2), 2.82–2.90 (2H, m, H-3, H_b-CH_2), 2.99–3.02 (1H, m, H-19), 3.67 (3H, s, $CO_2\underline{Me}$), 3.74–3.78 (1H, m, H-5′), 4.17–4.19 (1H, m, H_a-6′), 4.25–4.45 (3H, m, H_b-6′, CH_2N), 4.50–4.59 (4H, m, H-29, CH-OH, CH_2-O), 4.70 (1H, d, J = 8.0, H-1′), 4.73 (1H, s, H-29), 4.81 (1H, dd, J = 12.5, 2.5, H_a-CH_2N), 4.92 (1H, dd, J = 12.5, 6.0, H_b-CH_2N), 4.97–5.01 (1H, m, H-2′), 5.10 (1H, dt, J = 10.0, 2.5, H-4′), 5.22 (1H, t, J = 10, H-3′), 7.48, 7.50, 7.75, 7.76 (2H, 4 s, CH=C-N). ^{13}C NMR spectrum (δ, ppm, J/Hz): 14.7 (C-27), 15.9 (C-25), 16.3 (C-24), 16.9 (C-26), 18.5 (C-6), 19.4 (C-30), 20.5, 20.6, 20.7, 20.8 ($CO\underline{CH_3}$), 20.9 (C-11), 25.5 (C-12), 28.4 (C-23), 29.2 (=C-$\underline{CH_2}$), 29.6 (C-15), 30.6 (C-21), 32.2 (C-16), 34.2 (C-7), 35.7 (C-2), 36.9 (C-22), 37.4 (C-4), 38.2 (C-13), 39.2 (C-10), 40.7 (C-8), 42.4 (C-14), 45.4 (C-1), 47.0 (C-19), 49.5 (C-18), 50.4 (C-9), 51.3 ($CO_2\underline{Me}$), 53.2 (CH_2-N), 55.5 (C-5), 56.5 (C-17, CH_2-O), 61.8 (C-6′), 62.9 (CH_2-N), 68.3 (C-4′), 68.7 (CH-OH), 71.3 (C-2′), 71.9 (C-5′), 72.7 (C-3′), 82.2 (C-3), 99.9 (C-1′), 109.6 (C-29), 123.8, 123.9, 125.0 (CH=C-N), 143.8, 146.3, 146.4 (CH=C-N), 150.6 (C-20), 169.5, 169.6, 170.2, 170.8 ($\underline{C}OCH_3$), 176.7 (C-28). MS *m/z* 1059.6 $[M + Na]^+$ (calcd for $C_{54}H_{80}N_6O_{14}$, 1036.6).

2α-Methylene-{1*N*-1*H*-1,2,3-triazol-4-yl-[3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranos-1-yl)-methylene-1*H*-1,2,3-triazol-4-ylpropan-2-ol]}-3β-hydroxylup-20(29)-en-28-oic Acid (23). $C_{53}H_{78}N_6O_{14}$. Yield 53%, mp 144–146°C, $[\alpha]_D^{21}$ –17.4° (*c* 0.8, $CHCl_3$). IR spectrum ($CHCl_3$, ν, cm^{-1}): 1756 (C=O), 3446 (OH). ^1H NMR spectrum (δ, ppm, J/Hz): 0.79, 0.80, 0.91, 0.95, 0.97 (3H each, s, CH_3-23–27), 1.68 (3H, s, CH_3-30), 0.58–2.28 (23H, m, CH, CH_2 in pentacyclic skeleton), 2.01, 2.04, 2.09, 2.10 (3H each, s, $CO\underline{CH_3}$), 2.54–2.65 (1H, m, H_a-CH_2), 2.84–3.02 (3H, m, H-3, H_b-CH_2, H-19), 3.75–3.77 (1H, m, H-5′), 4.12–4.19 (1H, m, H_a-6′), 4.25–4.44 (3H, m, H_b-6′, CH_2N), 4.50–4.59 (4H, m, H-29, CH-OH, CH_2-O), 4.70 (1H, d, J = 8.5, H-1′), 4.72 (1H, s, H-29), 4.80 (1H, d, J = 12.5, H_a-CH_2N), 4.92 (1H, dd, J = 12.5, 1.5, H_b-CH_2N), 4.97–5.01 (1H, m, H-2′), 5.10 (1H, dt, J = 10.0, 1.5, H-4′), 5.22 (1H, t, J = 10, H-3′), 7.52, 7.76, 7.77 (2H, 3 s, CH=C-N). ^{13}C NMR spectrum (δ, ppm, J/Hz): 14.7 (C-27), 16.0 (C-25), 16.3 (C-24), 16.9 (C-26), 18.5 (C-6), 19.3 (C-30), 20.5, 20.6, 20.7, 20.8 ($CO\underline{CH_3}$), 20.9 (C-11), 25.4 (C-12), 28.4 (C-23), 29.2 (=C-$\underline{CH_2}$), 29.6 (C-15), 30.6 (C-21), 32.2 (C-16), 34.2 (C-7), 35.7 (C-2), 37.0 (C-22), 37.4 (C-4), 38.4 (C-13), 39.3 (C-10), 40.7 (C-8), 42.5 (C-14), 45.4 (C-1), 47.0 (C-19), 49.3 (C-18), 50.4 (C-9), 53.2 (CH_2-N), 55.5 (C-5), 56.3 (C-17, CH_2-O), 61.8 (C-6′), 62.8 (CH_2-N), 68.3 (C-4′), 68.7 (CH-OH), 71.3 (C-2′), 71.9 (C-5′), 72.7 (C-3′), 82.2 (C-3), 99.9 (C-1′), 109.6 (C-29), 123.8, 124.0, 125.0 (CH=C-N), 143.9, 146.3, 146.4 (CH=C-N), 150.5 (C-20), 169.5, 169.7, 170.3, 170.9 ($\underline{C}OCH_3$), 181.1 (C-28). MS *m/z* 1045.5 $[M + Na]^+$ (calcd for $C_{53}H_{78}N_6O_{14}$, 1022.6).

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