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Synthesis of water soluble glycosides of pentacyclic dihydroxytriterpene carboxylic acids as inhibitors of α-glucosidase

Jiancong Xu [a], Xuliang Nie [a], Yanping Hong [a,*], Yan Jiang [a], Guoqiang Wu [a], Xiaoli Yin [b], Chunrong Wang [a], Xiaoqiang Wang [a,c]

[a] Jiangxi Key Laboratory of Natural Product and Functional Food, College of Food Science and Engineering, Jiangxi Agricultural University, Nanchang 330045, China
[b] Library of Jiangxi Agricultural University, Nanchang 330045, China
[c] Department of Biological Sciences, University of North Texas, Denton, TX 76203, United States

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ABSTRACT

A series of compounds were synthesized by glycosylation of maslinic acid (MA) and corosolic acid (CA) with monosaccharides and disaccharides, and the structures of the derivatives were elucidated by standard spectroscopic methods including ^{1}H NMR, ^{13}C NMR and HRMS. The α-glucosidase inhibitory activities of all the novel compounds were evaluated *in vitro*. The solubility and inhibitory activity of α-glucosidase assays showed that the bis-disaccharide glycosides of triterpene acids possessed higher water solubility and α-glucosidase inhibitory activities than the bis-monosaccharide glycosides. Among these compounds, maslinic acid bis-lactoside (8e, IC_{50} = 684 μM) and corosolic acid bis-lactoside (9e, IC_{50} = 428 μM) had the best water solubility, and 9e exhibited a better inhibitory activity than acarbose (IC_{50} = 478 μM). However, most of glycosylated derivatives possessed lower inhibitory activities than the parent compounds, although their water solubility was enhanced obviously. Moreover, the kinetic inhibition studies indicated that 9e was a non-competitive inhibitor, and structure–activity relationships of the derivatives are also discussed.

1. Introduction

Diabetes mellitus affects approximately 382 million people worldwide according to the report of the International Diabetes Federation (IDF)[1] and type II diabetes mellitus accounts for the most. Therapy for the type II diabetes relies mainly on several approaches intended to suppress the hyperglycemia. It is effective to control elevated glucose level in blood through suppressing the activity of α-glucosidase,[2,3] glycogen phosphorylase (GP)[4,5] and protein tyrosine phosphatase-1B (PTP-1B).[6,7] α-Glucosidase is a membrane-bound enzyme at the epithelium of the small intestine, catalyzes the cleavage of glycosidic bonds in disaccharides and oligosaccharides and therefore gives rise to an increase blood glucose concentration. Inhibition of the activity of α-glucosidase is considered as an important means for managing type II diabetes.[8]

Maslinic acid (MA) and corosolic acid (CA) are triterpene acids found in a wide variety of plants such as *Olea europaea* L[9] and *Lagerstroemia* speciosa.[10] It is reported that MA[9] and CA[10–13] (Fig. 1) exhibited a glucose-lowering effect on postchallenge plasma glucose levels. Due to the rigid skeleton and hydrophobic structure, MA and CA do not dissolve well in water. Their poor water solubility and low bioavailability, however, are the key factors to limit their clinical applications as therapeutic agents. It has been demonstrated that encapsulation using cyclodextrins,[14,15] phosphorylation[16] and introduction of polar groups (e.g. glycosidic-[17]/amino acid-[18]/*N*-heterocyclic[19] residues) was an effective way to achieve enhancement of water solubility for triterpenoid compounds and other parent compounds. It has been reported that triterpenoid saponins synthesized or isolated from plants exhibit good water solubility and biological activities (e.g. antiviral activity,[20] antitumor activity,[21,22] anti-inflammatory activity[23]). In addition, the water solubility of the derivatives is tightly correlated with the number and the type of sugars in the glycosides, and it has been shown that the water solubility improvement may be an effective way to enhance the bioactivities of bioactive compounds.[18,24,25] So far, there have been only a few studies focused on the α-glucosidase inhibition properties of MA and CA derivatives. Here, we synthesized a series of glycoside derivatives of MA and CA by introducing the polar sugar moieties into their rigid skeleton at the C (2α)-OH and C (3β)-OH positions. They exhibited better water solubility than the parent compounds. Their α-glucosidase inhibitory activities were also evaluated. The results of the preliminary studies on the structure-activity relationship and the inhibitory mechanism have also been discussed.

* Corresponding author. Jiangxi Key Laboratory of Natural Product and Functional Food, College of Food Science and Engineering, Jiangxi Agricultural University, Nanchang 330045, China. Tel.: +86 791 83813863; fax: +86 791 83813863.
E-mail address: xyqcjx@163.com (Y. Hong).

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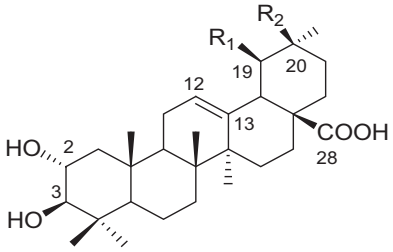


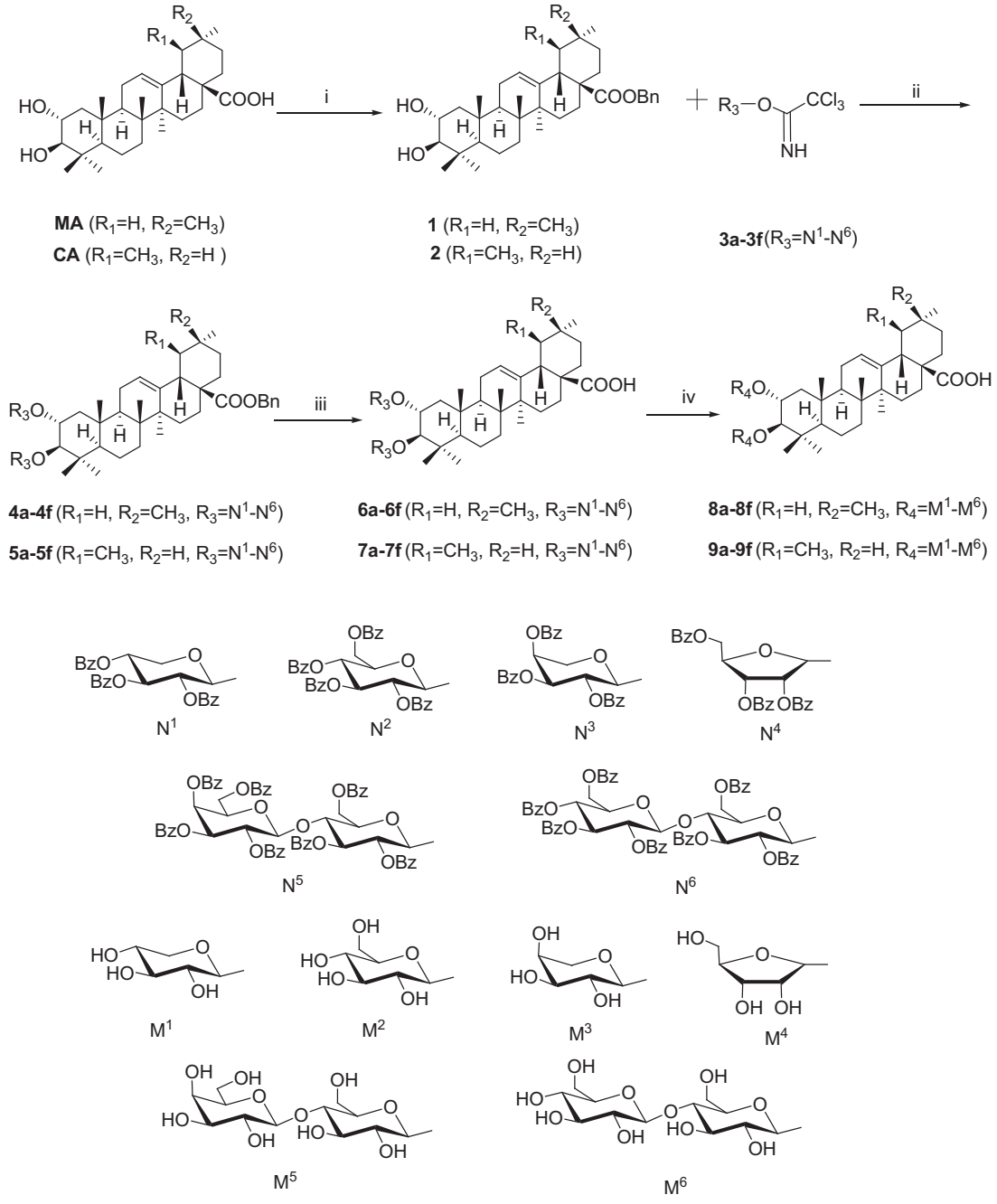
Fig. 1. The structures of maslinic acid and corosolic acid.

2. Results and discussion

2.1. Chemistry

MA and CA have three glycosylation sites, i.e. C (2α)-OH, C (3β)-OH and COOH (28β). It has been reported that the carboxyl group at C28 is very important for the hypoglycemic activity of these triterpenes.[26,27] Therefore, a series of derivatives were prepared by glycosylating MA and CA at C (2α)-OH and C (3β)-OH with D-glucose, D-xylose, L-arabinose, D-ribose, lactose and maltose, and the C28-carboxylic group unchanged. The synthetic route has been shown in Scheme 1.

Reagents and reaction conditions: (i) BnBr, K_2CO_3, DMF, 85 °C; (ii) TMSOTf, 4Å MS, CH_2Cl_2, rt; (iii) H_2, Pd-C (5%), EtOAc, reflux; (iv) NaOMe, MeOH, rt.



Scheme 1. Synthesis of 2α, 3β-diglycosides of maslinic acid (or corosolic acid).

The carboxyl group at C28 was critical for the hypoglycemic activity of these triterpenes, and benzyl (Bn) is already known to be an excellent protective group for COOH group.[28,29] Therefore, MA (or CA) was first converted into its benzyl ester 1 (or 2). The intermediate 4 (or 5) was prepared via glycosylation at C (2α)-OH and C (3β)-OH of 1 (or 2) with TMSOTf as catalyst according to a reported method.[30,31] However, the yield of 4 (or 5) with diglycosidic chains was less than 10%; large amounts of the by-product obtained was attributed to the regioselective reaction.[32] The result of thin layer chromatography showed that there were two main spots of product, and the ^{1}H NMR spectroscopic data indicated that the by-product was a mixture of monoglycosylated derivative of 1 (or 2) with only one sugar moiety at C (2α)-OH or C (3β)-OH, since the fourteen methyl and two hydroxyl distinct proton signals were observed. Therefore, the two by-products with single saccharide chain possessed a spot with the same value of R_f and the target product was the other spot in the TLC. The glycosylation reaction (ii) conditions were modified by ensuring stoichiometric excess of the saccharide donors and under a nitrogen atmosphere, and the yield of 4 (or 5) was enhanced from 10% to 50%. Then benzyl could be conveniently removed through catalytic hydrogenolysis in a high yield. Therefore, a series of derivatives with free carboxylic acids 6 and 7 were prepared. Finally, compounds 8 and 9 were synthesized by removal of the benzoyl protection through transesterification in NaOMe-MeOH. The structures of the intermediate and the final compounds were elucidated and confirmed by NMR spectral studies. In addition, the key NMR signals of typical derivatives with diglucosides (or monoglucosides) have been listed in Tables 1 and 2.

The ^{1}H NMR spectra of derivatives showed signals for hydrogens on the benzoyl (8.2–7.0 ppm), hydrogens on the sugar and the triterpenoid moieties (6.0–1.0 ppm), and seven methyl groups (<1.0 ppm). Due to the removal of benzyl group through catalytic hydrogenolysis, the integral values of the aromatic proton were changed between 4 (or 5) and 6 (or 7) at 5.0–4.9 ppm and 8.2–7.0 ppm concurrent with the disappearance of the benzylic methylene proton signals. The final products (8 and 9) had no proton absorption signals between 8.2 and 7.0 ppm with the removal of the benzoyl. The NMR data were generally consistent with those reported in the literature.[30]

With the introduction of the sugar moieties, the water solubility of these triterpene acids was improved dramatically. The water solubility of their derivatives is correlated with the number and type of sugars in the glycosides. Among the derivatives, the bis-disaccharide glycosides of triterpene acids could be dissolved in water completely due to the four polar sugar moieties in the two disaccharide chains. Although bis-monosaccharide glycosides of triterpene acids were less soluble than the bis-disaccharide glycosides, their water solubility is still much better than that of the parent compounds. When the concentration is less than 1 mg/mL, all the bis-monosaccharide glycosides of triterpene acids could disperse well in water except 8d and 9d (the ribosides). To prepare solutions of the derivatives with high concentrations, addition of a certain amount of ethanol into water was necessary. While 8b and 9b (the glucosides) dissolved completely in 10% ethanol, 8a and 9a (the xylosides) and 8c and 9c (the arabinosides) required 30% ethanol for complete dissolution. The worst water solubility was for 8d and 9d which could be dissolved completely in 50% ethanol.

Table 1
The key ^{1}H NMR signals of representative compounds (400 MHz, TMS, δ ppm)

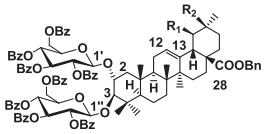
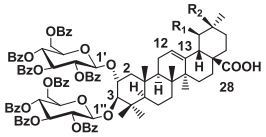
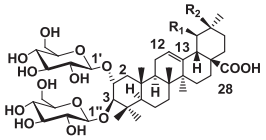
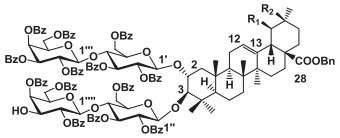
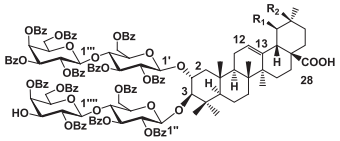
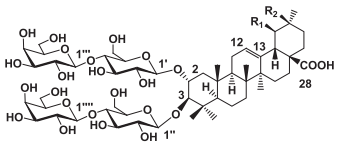
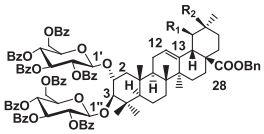
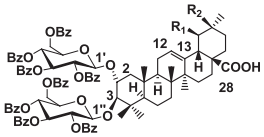
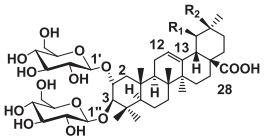
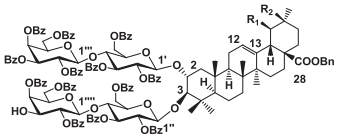
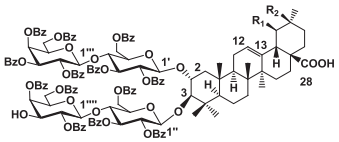
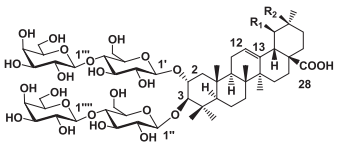
Compounds		H-C12	$PhCH_2$	H-C3	H-C2	H-anomeric carbon			
						1′	1″	1‴	1⁗
	4b ($CDCl_3$) R_1 = H, R_2 = CH_3	5.17-5.16	4.98-4.92	3.07	2.85	5.04-5.01	4.84-4.82		
	5b ($CDCl_3$) R_1 = CH_3, R_2 = H	5.14-5.12	4.93-4.88	3.07	2.21	5.14-5.02	4.85-4.82		
	6b ($CDCl_3$) R_1 = H, R_2 = CH_3	5.26-5.23		3.15	2.84	5.02	4.93-4.90		
	7b ($CDCl_3$) R_1 = CH_3, R_2 = H	5.24-5.22		3.15	2.21	5.01	4.95-4.92		
	8b (DMSO) R_1 = H, R_2 = CH_3	5.15		3.21	2.74-2.71	4.90	4.78-4.75		
	9b (DMSO) R_1 = CH_3, R_2 = H	5.13		3.20	2.13-2.10	4.90	4.78-4.76		
	4e ($CDCl_3$) R_1 = H, R_2 = CH_3	5.11-5.07	5.03-4.94	2.95	2.83	4.79-4.77	4.53-4.50	4.40-4.36	4.22-4.17
	5e ($CDCl_3$) R_1 = CH_3, R_2 = H	5.12-5.10	5.10-4.93	3.00	2.25	4.97-4.92	4.63-4.60	4.50-4.45	4.23
	6e ($CDCl_3$) R_1 = H, R_2 = CH_3	5.16-5.11		3.01	2.82-2.78	4.80-4.78	4.59-4.56	4.48-4.44	4.29-4.24
	7e ($CDCl_3$) R_1 = CH_3, R_2 = H	5.12		3.01	2.17	4.85	4.63-4.60	4.53-4.48	4.27-4.22
	8e (DMSO) R_1 = H, R_2 = CH_3	5.12		3.13-3.08	2.76-2.75	4.50-4.45	4.20-4.15	4.37-4.35	4.20-4.15
	9e (DMSO) R_1 = CH_3, R_2 = H	5.10		3.12-3.06	2.13-2.12	4.47	4.18-4.15	4.36	4.18-4.15

Table 2
The key ^{13}C NMR signals of representative compounds (100 MHz, TMS, δ ppm)

Compounds		C(28)	C(13)	C(12)	C(3)	C(2)	Anomeric carbon			
							1′	1″	1‴	1⁗
	4b($CDCl_3$) R_1 = H, R_2 = CH_3	177.3	143.7	122.0	89.3	65.9	97.4	101.6		
	5b($CDCl_3$) R_1 = CH_3, R_2 = H	177.1	138.3	125.1	89.0	66.0	97.7	101.7		
	6b($CDCl_3$) R_1 = H, R_2 = CH_3	184.0	143.6	122.1	89.2	64.2	97.3	101.6		
	7b($CDCl_3$) R_1 = CH_3, R_2 = H	183.8	138.0	125.2	88.9	64.2	97.5	101.6		
	8b(DMSO) R_1 = H, R_2 = CH_3	178.6	144.0	121.3	86.9	61.5	98.9	103.6		
	9b(DMSO) R_1 = CH_3, R_2 = H	178.3	138.3	124.4	87.1	61.6	98.7	103.6		
	4e($CDCl_3$) R_1 = H, R_2 = CH_3	177.3	143.4	122.1	89.4	65.9	98.5	102.1	100.7	100.9
	5e($CDCl_3$) R_1 = CH_3, R_2 = H	177.1	138.1	125.2	89.0	63.1	98.9	102.1	100.6	100.9
	6e($CDCl_3$) R_1 = H, R_2 = CH_3	183.0	143.3	122.2	89.3	67.3	98.4	102.0	100.8	100.9
	7e($CDCl_3$) R_1 = CH_3, R_2 = H	183.0	137.9	125.3	89.1	63.1	98.8	102.0	100.7	100.9
	8e(DMSO) R_1 = H, R_2 = CH_3	175.3	144.6	120.9	87.0	68.2	98.7	104.0	103.2	103.2
	9e(DMSO) R_1 = CH_3, R_2 = H	176.2	138.8	124.0	87.2	68.2	98.3	104.1	103.3	103.3

2.2. Bioactivity

In order to screen for the potent antidiabetic compounds which may be used in clinic, we chose the low toxicity ethanol–water system to dissolve samples instead of the common solvent (DMSO). However, unlike the derivatives, the parent compounds (MA and CA) could not be dissolved completely in the same solvent system and it was hard to perform the bioactivity assay for them and compare the inhibitory activity of α-glucosidase with the derivatives. Therefore, twelve glycosylated derivatives of pentacyclic dihydroxytriterpene acids, together with acarbose (as a positive control), were dissolved in ethanol–water (1:1) and their inhibitory activities against α-glucosidase were evaluated *in vitro*. In addition, we explored the effect of ethanol on α-glucosidase and found the activity of α-glucosidase was not affected when the volume of ethanol was less than 10% in the reaction mixture. To eliminate the influence from ethanol, we controlled the volume of ethanol added to the reaction system strictly. The results are summarized in Table 3. Because of the poor water solubility, 8d and 9d could not be dissolved well in ethanol–water (1:1) at high concentrations for determining their inhibitory activity. As shown in Table 3, most of the tested derivatives exhibited inhibitory activity, and the 8e (IC_{50} = 684 μM) and 9e (IC_{50} = 428 μM) glycosylated at C (2α)-OH and C (3β)-OH with lactose moiety showed the highest α-glucosidase inhibitory activity. Under the same experimental conditions, 9e exhibited lower IC_{50} than the positive control (acarbose, IC_{50} = 478 μM). On the other hand, the glycosides of CA showed better potency than the corresponding MA derivatives (e.g. 9e vs 8e; 9f vs 8f; 9b vs 8b). In addition, the inhibitory activity of α-glucosidase analysis indicated that the bis-disaccharide glycosides of the same triterpene acid possessed higher α-glucosidase inhibitory activities than the bis-monosaccharide glycosides (e.g. 8e vs 8a and 8b; 9e vs 9a and 9b). Both 8f (IC_{50} = 2940 μM) and 9f (IC_{50} = 2447 μM) were less active than 8e (IC_{50} = 684 μM) and 9e (IC_{50} = 428 μM), suggesting that the introduction of lactose group at C-2 and C-3 resulted in a better enhancement of water solubility and inhibitory activity. Among bis-monosaccharide glycosides of triterpene acids MA and CA, D-glucose group (9b, IC_{50} = 3437 μM) was the most favorite sugar moiety to be introduced for enhancing solubility and inhibitory activity (9b vs 9a, 9c and 9d).

To further analyze the inhibitory activities of α-glucosidase of the parent compounds and their derivatives under identical conditions, the parent compounds (MA, CA) and their derivatives with the highest α-glucosidase inhibitory activity (8e, 9e) and with the

Table 3
IC_{50} values (μM) of the final compounds for the inhibition of α-glucosidase

Compounds	IC_{50}[a]	Compounds	IC_{50}
8a	7865 ± 53	9a	5966 ± 21
8b	5362 ± 41	9b	3437 ± 17
8c	7837 ± 161	9c	7434 ± 6
8d	[b] NI	9d	NI
8e	684 ± 23	9e	428 ± 5
8f	2940 ± 6	9f	2447 ± 13
Acarbose	478 ± 5		

[a] Values are the mean of four experiments.
[b] NI = no inhibition.

Table 4
IC_{50} values (μM) of the final compounds (dissolved in DMSO) for the inhibition of α-glucosidase

Compounds	IC_{50}[a]	Compounds	IC_{50}
8e	705 ± 6	9e	448 ± 4
8d	[b]NI	9d	NI
MA	103 ± 1	CA	71 ± 1
Acarbose	449 ± 6		

[a] Values are the mean of four treatments.
[b] NI = no inhibition.

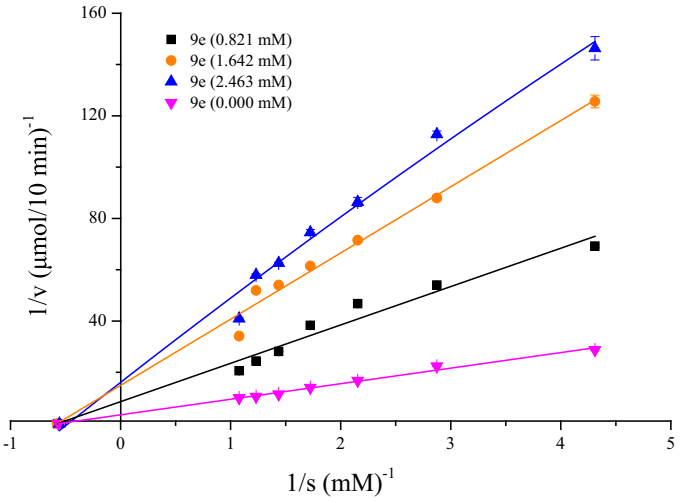


Fig. 2. Lineweaver–Burk plot of 9e.

worst water solubility (8d, 9d) were dissolved in DMSO. The α-glucosidase inhibitory activities were measured using the same method described above for α-glucosidase inhibition assay (ethanol–water system), and the results are presented in Table 4. MA (IC_{50} = 103 μM) and CA (IC_{50} = 71 μM) exhibited better activities than their derivatives. These indicated that introducing sugar moieties on the parent compounds by glycosylation can be detrimental to their α-glucosidase activity (e.g. MA vs 8e; CA vs 9e), although the water solubility of derivatives were enhanced obviously.

The kinetic studies were also further performed to explore the inhibition mechanism of the active compounds which inhibited the α-glucosidase. Considering the similarities in the structure of these derivatives, 9e with the highest inhibitory activity was selected for the kinetic analysis. The kinetic constants and modes of inhibition for 9e were determined based on Lineweaver–Burk plots (Fig. 2), and 9e exhibited a non-competitive inhibition mechanism because increasing substrate concentrations resulted in a series of lines with different slopes, but the same x-intercept. K_m (1.76 ± 0.02 mM) was obtained from the -(x) value at the intersection of the three straight lines.

3. Conclusion

In summary, a series of glycosylated derivatives of maslinic acid and corosolic acid with monosaccharides or disaccharides were synthesized and their α-glucosidase inhibitory activities were evaluated. Among all of the compounds, 9e (IC_{50} = 428 μM) with the best water solubility exhibited a better inhibitory activity than the positive reference (acarbose, IC_{50} = 478 μM). Analyses of the solubility and the inhibitory activities of α-glucosidase showed that the bis-disaccharide glycosides of triterpene acids possessed better water solubility and higher α-glucosidase inhibitory activities than the bis-monosaccharide glycosides. In addition, the derivatives of CA exhibited better inhibitory activity (IC_{50}) than the corresponding derivatives of MA. Moreover, the study of the kinetic inhibition indicated that the synthesized glycoside inhibitors (i.e., 9e) utilize a non-competitive inhibition mechanism. Glycosylation of the pentacyclic dihydroxytriterpene carboxylic acids (such as MA or CA) can improve their solubility obviously; however, the studies of α-glucosidase inhibition in vitro showed that the glycosylated derivatives possessed lower inhibitory activities than the parent compounds (MA or CA).

4. Experimental section

4.1. Chemicals and general methods

All chemicals and solvents used were of reagent grade. Boiling range of petroleum ether was 60–90 °C. Analytical TLC was performed on Merck silica-gel 60 F_{254} plates and spots were visualized with ultraviolet light (254 nm) followed by spraying with a solution of H_2SO_4 (10 mL) in ethanol (90 mL) and heating. The melting points were measured with Tektronix X4 microscopic melting point apparatus and are uncorrected. Optical rotations were determined with a Perkin-Elmer 241 polarimeter at room temperature. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 with the tetramethylsilane as inner reference. High resolution mass spectral analysis (HRMS) was performed on Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation). 4-Nitrophenyl-α-D-glucopyranoside (PNPG) and acarbose were purchased from Sigma. α-Glucosidase from *Saccharomyces cerevisiae* (product number: G5003, CAS: 9001-42-7) was also purchased from Sigma.

4.2. Synthesis

4.2.1. Saccharide donors (3) were prepared according to the reported methods[33–35]

Maslinic acid, corosolic acid, benzyl-2α, 3β-dihydroxyolean-12-en-28-oic acid (1) and benzyl-2α, 3β-dihydroxyurs-12-en-28-oic acid (2) were synthesized by using the reported methods.[13,36]

4.2.2. 2-α,3-β-di-(2, 3, 4-tri-O-benzoyl-xylosyloxy)-benzyl maslinate (4a)

Powdered 4Å molecular sieves (500 mg) and TMSOTf (50 μL) were added to a solution of 3a (xylosyl trichloroacetimidate, 2.40 g, 3.95 mmol) in dry CH_2Cl_2 at rt while stirring. The reaction mixture was stirred for 5 min followed by addition of 1 (1.00 g, 1.80 mmol) under the nitrogen atmosphere. After 2 h, Et_3N (0.20 mL) was added to terminate the reaction. The mixture was then filtered and the filtrate was concentrated and purified by a silica gel-column chromatography (6:1, petroleum ether-EtOAc) to give 4a as a white solid (1.41 g, 67.5%). $[\alpha]_D^{25} = -18°$ (c = 0.1, $CDCl_3$); mp: 150–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.98 (m, 5H), 7.94–7.83 (m, 10H), 7.50–7.29 (m, 16H), 7.24–7.18 (m, 4H), 5.87 (t, 1H, *J* = 9.3 Hz), 5.69 (t, 1H, *J* = 6.3 Hz), 5.39–5.36 (m, 4H), 5.20–5.15 (m, 1H), 5.04–4.95 (m, 3H), 4.84–4.81 (m, 2H), 4.42–4.37 (m, 1H), 3.89–3.80 (m, 2H), 3.60 (t, 1H, *J* = 10.5 Hz), 3.09 (d, 1H, *J* = 9.3 Hz), 2.85 (d, 1H, *J* = 12.1 Hz), 1.97–1.95 (m, 1H), 1.90–1.84 (m, 1H), 1.79–1.70 (m, 3H), 1.62–1.56 (m, 3H), 1.51–1.46 (m, 2H), 1.36–1.34 (m, 1H), 1.32–1.28 (m, 2H), 1.16–1.04 (m, 7H), 0.90 (s, 3H), 0.88 (s, 3H), 0.84 (s, 3H), 0.79 (s, 6H), 0.55 (s, 3H), 0.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 165.8, 165.7, 165.4, 165.3, 165.2, 164.9, 143.6, 136.3, 133.4, 133.3, 133.1, 133.0, 129.9, 129.8, 129.7, 129.5, 129.4, 129.1, 129.0, 128.3, 128.2,128.1, 128.0, 127.9, 122.0,101.0, 99.0, 89.2, 74.7, 72.4, 72.2, 70.2, 69.0, 68.4, 67.9, 65.9, 63.1, 61.2, 54.6, 47.2, 46.6, 46.0, 44.3, 41.6, 41.3, 40.7, 39.1,

37.3, 33.8, 33.1, 32.4, 32.2, 30.6, 28.3, 27.4, 26.8, 25.4, 23.7, 23.4, 22.9, 18.0, 17.5, 16.7, 16.3.

4.2.3. 2-α,3-β-di-(2, 3, 4, 6-tetra-O-benzoyl-glucosyloxy)-benzyl maslinate (4b)

It was prepared as a white solid from 1 and 3b (glucosyl trichloroacetimidate) by using the method established for 4a (1.56 g, 51%). $[\alpha]_D^{25}$ = +55° (c = 0.1, $CDCl_3$); mp: 143–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–7.92 (m, 6H), 7.86–7.80 (m, 6H), 7.76–7.74 (m, 4H), 7.43–7.30 (m, 10H), 7.28–7.13 (m, 19H), 5.93–5.86 (m, 2H), 5.80–5.74 (m, 2H), 5.58 (t, 1H, *J* = 7.7 Hz), 5.49 (t, 1H, *J* = 7.9 Hz), 5.20–5.14 (m, 2H), 5.04–4.92 (m, 3H), 4.84–4.82 (m, 1H), 4.68–4.63 (m, 2H), 4.56–4.52 (m, 1H), 4.38–4.32 (m, 1H), 4.22–4.13 (m, 1H), 4.10–4.0 (m, 1H), 3.07 (d, 1H, *J* = 8.9 Hz), 2.85 (d, 1H, *J* = 13.1 Hz), 2.00 (d, 1H, *J* = 10.6 Hz), 1.87 (t, 1H, *J* = 13.1 Hz), 1.68–1.47 (m, 9H), 1.30–1.03 (m, 9H), 0.89 (s, 6H), 0.87 (s, 3H), 0.71 (s, 6H), 0.60 (s, 3H), 0.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 166.1, 165.9, 165.8, 165.2, 165.1, 165.0, 143.7, 136.3, 133.2, 133.0, 132.9, 132.8, 132.7, 129.9, 129.8, 129.7, 129.6, 129.2, 129.1, 129.0, 128.4, 128.3, 128.2, 128.1, 127.9, 122.0, 101.6, 97.4, 89.2, 73.7, 73.6, 73.4, 73.2, 72.7, 72.4, 71.3, 70.8, 70.2, 65.9, 64.2, 63.7, 54.5, 47.3, 46.6, 45.9, 43.1, 41.6, 41.3, 40.1, 39.1, 37.2, 33.8, 33.1, 32.3, 32.3, 30.6, 28.4, 27.4, 25.6, 23.7, 23.4, 23.0, 18.0.

4.2.4. 2-α,3-β-di-(2, 3, 4-tri-O-benzoyl-arabinosyloxy)-benzyl maslinate (4c)

It was prepared as a white solid from 1 and 3c (arabinosyl trichloroacetimidate) and by using the method established for 4a (1.65 g, 63.2%). $[\alpha]_D^{25}$ = +109° (c = 0.1, $CDCl_3$); mp: 160–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.92 (m, 7H), 7.83–7.79 (m, 4H), 7.76–7.74 (m, 2H), 7.46–7.39 (m, 8H), 7.34–7.30 (m, 5H), 7.24–7.18 (m, 9H), 5.72 (t, 1H, *J* = 8.7 Hz), 5.63–5.49 (m, 6H), 5.20 (s, 1H), 5.01–4.95 (m, 3H), 4.80 (d, 1H, *J* = 7.6 Hz), 4.60–4.53 (m, 1H), 4.26 (d, 1H, *J* = 13.4 Hz), 4.01–3.93 (m, 2H), 3.83 (d, 1H, *J* = 13.3 Hz), 3.07 (d, 1H, *J* = 9.3 Hz), 2.86 (d, 1H, *J* = 13.1 Hz), 2.03–1.97 (m, 1H), 1.87–1.83 (m, 1H), 1.72–1.68 (m, 2H), 1.64–1.56 (m, 4H), 1.51–1.45 (m, 2H), 1.35 (s, 1H), 1.30–1.27 (m, 2H), 1.15–1.03 (m, 7H), 0.90 (s, 3H), 0.88 (s, 3H), 0.83 (s, 3H), 0.79 (s, 3H), 0.74 (s, 3H), 0.61 (s, 3H), 0.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 165.7, 165.6, 165.5, 165.3, 165.2, 143.7, 136.3, 133.3, 133.2, 133.1, 133.0, 132.9, 130.0, 129.8, 129.7, 129.6, 129.5, 129.4, 129.1, 128.9, 128.4, 128.3, 128.1, 128.0, 127.9, 122.0, 101.2, 98.7, 90.1, 75.0, 71.4, 70.7, 70.4, 69.2, 67.7, 65.9, 64.2, 54.6, 47.2, 46.6, 46.0, 44.1, 41.6, 41.4, 40.5, 39.1, 37.2, 33.8, 33.1, 32.4, 32.2, 30.6, 28.4, 27.3., 26.8, 25.4, 23.7, 23.4, 23.0, 18.0, 17.7, 16.7, 16.2.

4.2.5. 2-α,3-β-di-(2, 3, 5-tri-O-benzoyl-ribosyloxy)-benzyl maslinate (4d)

It was prepared as a white solid from 1 and 3d (ribosyl trichloroacetimidate) by using the method established for 4a (1.37 g, 57.1%). $[\alpha]_D^{25}$ = −40° (c = 0.1, $CDCl_3$); mp: 161–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.96 (m, 10H), 7.81–7.77 (m, 2H), 7.56–7.37 (m, 9H), 7.34–7.27 (m, 10H), 7.25–7.21 (m, 4H), 6.17 (s, 1H), 6.08 (s, 1H), 5.67 (s, 2H), 5.55 (s, 1H), 5.45 (s, 2H), 5.27 (d, 2H, *J* = 16.4 Hz), 5.09–5.01 (m, 2H), 4.72 (d, 1H, *J* = 12.5 Hz), 4.59 (d, 1H, *J* = 10.0 Hz), 4.22–4.18 (m, 1H), 4.09 (d, 1H, *J* = 12.6 Hz), 4.00–3.96 (m, 1H), 3.42 (d, 1H, *J* = 9.4 Hz), 2.90 (d, 1H, *J* = 12.4 Hz), 2.19 (d, 1H, *J* = 10.0 Hz), 2.00–1.94 (m, 1H), 1.88–1.86 (m. 2H), 1.72–1.54 (m, 9H), 1.43–1.38 (m, 2H), 1.33–1.25 (m, 3H), 1.15 (s, 3H), 1.09 (s, 3H), 0.93 (s, 3H), 0.91 (s, 3H), 0.89 (s, 3H), 0.77 (s, 3H), 0.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1, 166.1, 166.0, 165.5, 165.3, 165.0, 143.7, 136.3, 133.2, 132.9, 132.8, 130.2, 130.0, 129.9, 129.8, 129.7, 129.6, 128.4, 128.3, 128.2, 128.0, 127.9, 122.1, 101.0, 93.8, 89.6, 70.7, 69.6, 69.4, 68.3, 68.1, 67.5, 66.3, 65.9, 62.4, 61.6, 55.0, 47.5, 46.7, 45.8, 42.3, 41.4, 40.7, 39.3, 37.5, 33.8, 33.1, 32.6, 32.3, 30.6, 28.5, 26.9, 25.7, 23.6, 23.4, 23.0, 18.2, 17.5, 16.8, 16.4.

4.2.6. 2-α,3-β-di-(2, 3, 4, 6, 2', 3', 4', 6'-octa-O-benzoyl-lactosyloxy)-benzyl maslinate (4e)

It was prepared as a white solid from 1 and 3e (lactosyl trichloroacetimidate) by using the method established for 4a (1.46 g, 50.6%). $[\alpha]_D^{25}$ = +38° (c = 0.1, $CDCl_3$); mp: 171–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.06 (m, 2H), 7.97–7.79 (m, 25H), 7.70–7.66 (m, 4H), 7.58–7.31 (m, 28H), 7.20–7.09 (m, 16H), 5.73–5.62 (m, 6H), 5.44–5.36 (m, 2H), 5.32–5.30 (m, 1H), 5.27–5.22 (m, 1H), 5.11–5.07 (m, 1H), 5.03–4.94 (m, 2H), 4.79–4.64 (m, 6H), 4.53–4.50 (m, 1H), 4.40–4.36 (m, 1H). 4.20 (t, 1H, *J* = 9.2 Hz), 3.89–3.83 (m, 4H), 3.70 (m, 4H), 3.82 (m, 1H), 3.35 (t, 1H, *J* = 11.7 Hz), 2.95 (d, 1H, *J* = 9.0 Hz), 2.83 (d, 1H, *J* = 11.6 Hz), 1.86–1.73 (m, 5H), 1.65–1.55 (m, 4H), 1.47–1.40 (m, 3H), 1.24–1.18 (m, 2H), 1.10–0.99 (m, 2H), 0.90 (s, 3H), 0.88 (s, 3H), 0.83 (s, 3H), 0.68 (s, 3H), 0.61 (s, 3H), 0.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 165.9, 165.8, 165.4, 165.2, 164.9, 164.7, 143.4, 136.3, 133.4, 133.2, 133.1, 133.0, 132.8, 130.1, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 122.1, 102.1, 100.7, 98.5, 89.4, 75.9, 74.1, 73.6, 73.2, 72.9, 72.7, 72.0, 71.8, 71.7, 71.1, 70.8, 69.9, 67.5, 67.3, 65.9, 63.1, 60.7, 60.2, 54.5, 47.2, 46.6, 44.0, 41.6, 41.3, 40.3, 39.1, 37.1, 33.1, 32.3, 30.6, 28.2, 27.4, 25.5, 23.7, 23.2, 22.9, 17.9, 17.4, 16.6, 16.1.

4.2.7. 2-α,3-β-di-(2, 3, 4, 6, 2', 3', 4', 6'-octa-O-benzoyl-maltosyloxy)-benzyl maslinate (4f)

It was prepared as a white solid from 1 and 3f (maltosyl trichloroacetimidate) by using the method established for 4a (1.75 g, 52.1%). $[\alpha]_D^{25}$ = +56° (c = 0.1, $CDCl_3$); mp: 158–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23–8.21 (m, 2H), 8.16–8.13 (m, 2H), 8.05–8.00 (m, 4H), 7.89–7.87 (m, 2H), 7.84–7.83 (m, 2H), 7.79–7.76 (m, 5H), 7.73–7.70 (m, 7H), 7.63–7.61 (m, 2H), 7.54–7.45 (m, 6H), 7.43–7.37 (m, 15H), 7.36–7.28 (m, 13H), 7.25–7.22 (m, 6H), 7.20–7.16 (m, 5H), 7.15–7.11 (m, 4H), 6.14–6.05 (m, 2H), 5.79–5.73 (m, 2H), 5.71–5.63 (m, 3H), 5.51 (d, 1H, *J* = 3.8 Hz), 5.43–5.39 (m, 1H), 5.31–5.22 (m, 4H), 5.11–4.94 (m, 6H), 4.85 (d, 1H, *J* = 7.8 Hz), 4.69–4.65 (m, 1H), 4.63–4.56 (m, 3H), 4.50–4.47 (m, 1H), 4.44–4.40 (m, 1H), 4.33–4.28 (m, 2H), 4.25–4.22 (m, 1H), 4.19–4.10 (m, 2H), 3.96–3.90 (m, 1H), 3.06 (d, 1H, *J* = 9.3 Hz), 2.93–2.88 (m, 1H), 1.97–1.90 (m, 2H), 1.76–1.72 (m, 1H), 1.69–1.60 (m, 7H), 1.56–1.53 (m, 2H), 1.34–1.27 (m, 2H), 1.25–1.16 (m, 4H), 1.13–1.08 (m, 2H), 0.96 (s, 3H), 0.93 (s, 6H), 0.74 (s, 3H), 0.72 (s, 3H), 0.54 (s, 3H), 0.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.3, 166.2, 166.1, 165.9, 165.7, 165.6, 165.5, 165.4, 165.1, 165.0, 164.9, 164.8, 143.6, 136.3, 133.4, 133.2, 133.1, 133.0, 132.9, 132.8, 132.7, 130.1, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 122.1, 101.6, 97.3, 97.0, 96.1, 89.0, 75.6, 75.2, 75.1, 73.7, 73.4, 72.5, 70.9, 70.8, 70.1, 69.1, 68.7, 65.9, 64.3, 62.5, 62.4, 54.5, 47.3, 46.7, 45.9, 43.4, 41.6, 41.3, 40.2, 39.1, 37.2, 33.8, 33.1, 32.4, 32.3, 30.6, 28.4, 27.4, 25.6, 23.7, 23.4, 23.0, 18.0, 17.5, 16.7, 16.2.

4.2.8. 2-α,3-β-di-(2, 3, 4-tri-O-benzoyl-xylosyloxy)-benzyl corosolate (5a)

It was prepared as a white solid from 2 and 3a by using the method established for 4a (1.37 g, 65.6%). $[\alpha]_D^{25}$ = −27° (c = 0.1, $CDCl_3$); mp: 153–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–8.00 (m, 4H), 7.94–7.85 (m, 8H), 7.51–7.27 (m, 16H), 7.25–7.16 (m, 7H), 5.85 (t, 1H, *J* = 9.3 Hz), 5.70–5.65 (m, 1H), 5.40–5.33 (m, 1H), 5.14 (s, 1H), 5.07–5.01 (m, 1H), 4.97 (s, 1H), 4.90–4.81 (m, 3H), 4.41–4.37 (m, 1H), 3.89–3.80 (m, 2H), 3.59 (t, 1H, *J* = 10.4 Hz), 3.09 (d, 1H, *J* = 9.3 Hz), 2.20 (d, 1H, *J* = 10.9 Hz), 1.98–1.74 (m, 3H), 1.70–1.52 (m, 7H), 1.43–1.40 (m, 1H), 1.35–1.09 (m, 9H), 0.89 (s, 3H), 0.82 (s, 12H), 0.56 (s, 3H), 0.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ 177.2, 165.8, 165.7, 165.4, 165.3, 164.9, 138.5, 136.3, 133.3, 133.2, 133.1, 133.0, 130.1, 130.0, 129.9, 129.8, 129.6, 129.5, 129.2, 128.4, 128.3, 128.2, 128.1, 128.0, 125.1, 101.0, 99.1, 89.1, 74.7, 72.5, 12.0, 70.4, 70.3, 70.2, 69.5, 66.0, 63.2, 61.2, 54.7, 52.8, 48.0, 47.3, 44.2, 42.0, 40.9, 39.5, 39.1, 38.8,

37.5, 36.6, 32.7, 30.6, 28.4, 27.9, 24.1, 23.4, 23.3, 21.2, 18.1, 17.5, 17.2, 16.9, 16.6.

4.2.9. 2-α,3-β-di-(2, 3, 4, 6-tetra-O-benzoyl-glucosyloxy)-benzyl corosolate (5b)

It was prepared as a white solid from 2 and 3b by using the method established for 4a (1.71 g, 55.2%). $[\alpha]_D^{25} = +60°$ (c = 0.1, $CDCl_3$); mp: 134–135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.90 (m, 6H), 7.86–7.84 (m, 4H), 7.81–7.79 (m, 2H), 7.75–7.73 (m, 4H), 7.44–7.36 (m, 5H), 7.35–7.27 (m, 9H), 7.25–7.08 (m, 15H), 5.92–5.85 (m, 2H), 5.80–5.73 (m, 2H), 5.59–5.49 (m, 2H), 5.20–5.10 (m, 2H), 5.06–5.00 (m, 1H), 4.93–4.82 (m, 3H), 4.70–4.53 (m, 3H), 4.37–4.28 (m, 1H), 4.2–4.14 (m, 1H), 4.05–3.99 (m, 1H), 3.07 (d, 1H, *J* = 9.2 Hz), 2.21 (d, 1H, *J* = 11.1 Hz), 2.01–1.87 (m, 2H), 1.75–1.55 (m, 8H), 1.44–1.41 (m, 1H), 1.24–1.08 (m, 9H), 0.90 (s, 3H), 0.85 (s, 6H), 0.72 (s, 6H), 0.58 (s, 3H), 0.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 166.2, 166.1, 165.9, 165.3, 165.1, 165.0, 138.3, 136.3, 133.2, 133.1, 133.0, 132.8, 132.7, 129.9, 129.8, 129.7, 129.6, 129.3, 129.1, 129.0, 128.4, 128.3, 128.2, 128.1, 128.0, 125.2, 101.7, 97.8, 89.0, 73.9, 73.6, 73.4, 73.3, 71.4, 70.9, 70.3, 66.0, 64.2, 63.8, 54.6, 52.8, 48.0, 47.4, 43.3, 42.0, 40.3, 39.4, 39.1, 38.8, 37.3, 36.6, 32.6, 30.6, 28.4, 27.8, 24.1, 23.4, 23.2, 21.1, 18.0, 17.6, 17.1, 16.8, 16.4.

4.2.10. 2-α,3-β-di-(2, 3, 4-tri-O-benzoyl-arabinosyloxy)-benzyl corosolate (5c)

It was prepared as a white solid from 2 and 3c by using the method established for 4a (1.80 g, 69.0%). $[\alpha]_D^{25} = +120°$ (c = 0.1, $CDCl_3$); mp: 163–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.91 (m, 6H), 7.81–7.76 (m, 4H), 7.73–7.71 (m, 2H), 7.46–7.35 (m, 7H), 7.33–7.29 (m, 6H), 7.25–7.18 (m, 10H), 5.72 (t, 1H, *J* = 8.7 Hz), 5.58–5.50 (m, 5H), 5.16 (s, 1H), 5.06–5.01 (m, 1H), 4.95–4.88 (m, 2H), 4.79 (d, 1H, *J* = 7.5 Hz), 4.65–4.56 (m, 2H), 4.25 (d, 1H, *J* = 13.4 Hz), 4.01–3.93 (m, 2H), 3.82 (d, 1H, *J* = 13.4 Hz), 3.07 (d, 1H, *J* = 9.3 Hz), 2.21 (d, 1H, *J* = 11.1 Hz), 2.04–2.00 (m, 1H), 1.90–1.54 (m, 9H), 1.44–1.08 (m, 8H), 0.89 (s, 3H),0.82 (s, 9H), 0.75 (s, 3H), 0.61 (s, 3H), 0.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1, 165.6, 165.4, 165.3, 165.2, 138.5, 136.2, 133.3, 133.2, 133.1, 133.0, 132.9, 130.0, 129.7,129.6, 129.5, 129.4, 129.3, 129.1, 128.9, 128.3, 128.1, 128.0, 127.9, 125.0, 101.1, 98.7, 90.2, 74.9, 71.4, 70.7, 70.2, 69.2, 67.6, 65.9, 64.2, 54.6, 52.8, 47.9, 47.2, 43.9, 41.9, 40.6, 38.8, 37.4, 36.5, 32.6, 30.5, 28.4, 27.8, 26.8, 24.0, 23.4, 23.3, 21.1, 18.1, 17.6, 17.2, 16.8, 16.5.

4.2.11. 2-α,3-β-di-(2, 3, 5-tri-O-benzoyl-ribosyloxy)-benzyl corosolate (5d)

It was prepared as a white solid from 2 and 3d by using the method established for 4a (1.71 g, 64.0%). $[\alpha]_D^{25} = -53°$ (c = 0.1, $CDCl_3$); mp: 161–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.96 (m, 4H), 7.93–7.91 (m, 6H), 7.74–7.72 (m, 2H), 7.52–7.33 (m, 9H), 7.30–7.26 (m, 2H), 7.25–7.17 (m, 12H), 6.12 (s, 1H), 6.03 (s, 1H), 5.61 (s, 2H), 5.49 (s, 1H), 5.41 (s, 2H) 6.03 (s, 1H), 5.61 (s, 2H), 5.49 (s, 1H), 5.41 (s, 2H), 5.24 (s, 1H), 5.15 (s, 1H), 5.07–5.01 (m, 1H), 4.93–4.88 (m, 1H), 4.67 (d, 1H, *J* = 12.7 Hz), 4.53 (d, 1H, *J* = 11.0 Hz), 4.17–4.12 (m, 1H), 4.04 (d, 1H, *J* = 12.4 Hz), 3.96–3.88 (m, 1H), 3.37 (d, 1H, *J* = 9.5 Hz), 2.23–2.12 (m, 2H), 1.96–1.55 (m, 9H), 1.47–1.37 (m, 5H), 1.35–1.17 (m, 5H), 1.10 (s, 3H), 0.99 (s, 3H), 0.88 (s, 6H), 0.81 (s, 3H), 0.72 (s, 3H), 0.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 166.1, 165.5, 165.3, 165.0, 138.2, 136.3, 133.2, 133.1, 133.0, 132.8, 130.2, 130.0, 129.9, 129.8, 129.7, 129.6, 128.4, 128.3, 128.2, 128.1, 127.9, 125.3, 101.0, 93.8, 89.5, 70.6, 69.6, 69.4, 68.3, 68.1, 67.5, 66.2, 65.9, 62.4, 61.6, 55.0, 52.8, 48.0, 47.5, 42.4, 42.0, 40.7, 39.5, 39.0, 38.8, 37.5, 36.6, 32.8, 30.6, 28.6, 26.8, 24.2, 23.4, 23.3, 21.1, 18.2, 17.6, 17.0, 16.9, 16.5.

4.2.12. 2-α,3-β-di-(2, 3, 4, 6, 2', 3', 4', 6'-octa-O-benzoyl-lactosyloxy)-benzyl corosolate (5e)

It was prepared as a white solid from 2 and 3e by using the method established for 4a (2.8 g, 44.5%). $[\alpha]_D^{25} = +50°$ (c = 0.1, $CDCl_3$); mp: 172–173 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13–8.11 (m, 2H), 8.04–8.02 (m, 2H), 8.01–7.92 (m, 15H), 7.92–7.84 (m, 6H), 7.76–7.72 (m, 4H), 7.64–7.54 (m, 4H), 7.53–7.43 (m, 13H), 7.41–7.28 (m, 20H), 7.24–7.16 (m, 9H), 5.77–5.68 (m, 6H), 5.50–5.29 (m, 4H), 5.12–5.07 (m, 2H), 4.97–4.92 (m, 1H), 4.83–4.60 (m, 7H), 4.50–4.45 (m, 1H), 4.23 (t, 1H, *J* = 9.3 Hz), 3.92–3.64 (m, 9H), 3.42–3.37 (m, 1H), 3.00 (d, 1H, *J* = 9.2 Hz), 2.25 (d, 1H, *J* = 11.0 Hz), 2.00–1.85 (m, 2H), 1.69–1.61 (m, 8H), 1.55–1.43 (m, 3H), 1.27–1.09 (m, 7H), 0.96 (s, 3H), 0.87 (s, 6H), 0.75 (s, 3H), 0.69 (s, 3H), 0.49 (s, 3H), 0.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1, 165.8, 165.4, 165.3, 165.2, 164.9, 164.6, 138.1, 136.2, 133.4, 133.2, 133.1, 133.0, 132.9, 132.8, 130.2, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 125.2, 102.1, 100.9, 100.6, 98.9, 89.0, 76.0, 74.3, 73.6, 73.4, 73.2, 72.8, 71.9, 71.8, 71.7, 71.0, 70.8, 69.9, 69.8, 67.4, 67.2, 65.9, 63.1, 60.6, 60.2, 54.5, 52.7, 48.0, 47.3, 44.2, 41.8, 40.4, 39.3, 39.0, 38.8, 37.1, 36.5, 32.6, 30.6, 28.2, 27.7, 24.1, 23.3, 23.0, 21.1, 17.9, 17.2, 17.0, 16.7, 16.3.

4.2.13. 2-α,3-β-di-(2, 3, 4, 6, 2', 3', 4', 6'-octa-O-benzoyl-maltosyloxy)-benzyl corosolate (5f)

It was prepared as a white solid from 2 and 3f by using the method established for 4a (1.92 g, 50.0%). $[\alpha]_D^{25} = +48°$ (c = 0.1, $CDCl_3$); mp: 156–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12–8.06 (m, 2H), 8.04–7.96 (m, 2H), 7.92–7.87 (m, 4H), 7.76–7.73 (m, 2H), 7.72–7.68 (m, 2H), 7.66–7.55 (m, 13H), 7.46–7.44 (m, 2H), 7.40–7.31 (m, 8H), 7.25–6.97 (m, 40H), 5.99–5.91 (m, 2H), 5.64–5.49 (m, 5H), 5.37–5.33 (m, 1H), 5.28 (t, 1H, *J* = 8.1 Hz), 5.16–5.05 (m, 4H), 4.98–4.79 (m, 6H), 4.71 (d, 1H, *J* = 7.8 Hz), 4.57–4.53 (m, 1H), 4.47–4.38 (m, 3H), 4.35–4.33 (m, 1H), 4.28–4.26 (m, 1H), 4.19–4.15 (m, 2H), 4.08–3.99 (m, 3H), 3.80–3.74 (m, 1H), 2.92 (d, 1H, *J* = 9.3 Hz), 2.13 (d, 1H, *J* = 11.2 Hz), 1.85–1.79 (m, 2H), 1.65–1.48 (m, 9H), 1.36 (d, 1H, *J* = 11.1 Hz), 1.16–1.09 (m, 6H), 1.01–0.97 (m, 2H), 0.83 (s, 3H), 0.76 (s, 6H), 0.61 (s, 6H), 0.39 (s, 3H), 0.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1, 166.2, 166.1, 165.8, 165.7, 165.6, 165.5, 165.4, 165.1, 165.0, 164.9, 164.8, 138.2, 136.3, 133.4, 133.2, 133.2, 133.1, 133.0, 132.9, 132.8, 132.7, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 125.2, 101.6, 97.6, 96.9, 96.1, 88.8, 75.6, 75.2, 74.9, 74.0, 73.5, 73.4, 73.3, 72.5, 72.4, 71.2, 70.9, 70.8, 70.1, 69.1, 69.0, 68.7, 65.9, 64.2, 62.4, 54.5, 52.8, 48.0, 47.3, 43.5, 41.9, 40.3, 39.4, 39.0, 38.8, 37.2, 36.5, 32.6, 30.6, 28.3, 27.8, 24.1, 23.4, 23.2, 21.1, 18.0, 17.4, 17.0, 16.8, 16.4.

4.2.14. 2-α,3-β-di-(2, 3, 4-tri-O-benzoyl-xylosyloxy)-maslinic acid (6a)

A mixture of 4a (1.33 g, 0.92 mmol) and 5% Pd/C (0.80 g) in EtOAc (50 mL) was stirred at 85 °C under H_2 at atmospheric pressure for 4 h. The reaction mixture was filtered and concentrated in vacuo to give 6a as a white solid (1.1 g, 88.0%). $[\alpha]_D^{25} = -19°$ (c = 0.1, $CDCl_3$); mp: 184–186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11–8.09 (m, 2H), 8.07–8.05 (m, 2H), 8.01–7.99 (m, 2H), 7.96–7.93 (m, 6H), 7.57–7.53 (m, 1H), 7.52–7.45 (m, 4H), 7.44–7.42 (m, 2H), 7.40–7.37 (m, 4H), 7.35–7.33 (m, 3H), 7.32–7.30 (m, 2H), 7.28–7.27 (m, 1H), 7.25–7.24 (m, 1H), 5.97–5.92 (m, 1H), 5.79–5.75 (m, 1H), 5.50–5.44 (m, 3H), 5.25–5.19 (m, 1H), 5.10–5.05 (m, 1H), 4.94–4.88 (m, 2H), 4.48–4.44 (m, 1H), 4.13–4.08 (m, 1H), 3.92–3.89 (m, 2H), 3.69–3.64 (m, 1H), 3.18–3.15 (m, 1H), 2.83 (d, 1H, *J* = 13.6 Hz), 2.04–2.00 (m, 2H), 1.93–1.88 (m, 1H), 1.86–1.70 (m, 2H), 1.66–1.55 (m, 5H), 1.41–1.35 (m, 2H), 1.29–1.21 (m, 4H), 1.19–1.07 (m, 4H), 0.97 (s, 3H), 0.95 (s, 3H), 0.91 (s, 3H), 0.87 (s, 3H), 0.85 (s, 3H), 0.65 (s, 3H), 0.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.8, 165.8, 165.7, 165.4, 165.3, 164.9, 143.5, 133.3, 133.2, 133.1, 133.0, 129.8, 129.7, 129.6, 129.4, 129.1, 129.0, 128.3, 128.2, 128.0, 122.1, 100.9, 99.1, 89.2, 74.7, 72.4, 72.2, 70.3, 70.2, 70.1, 69.4, 63.1, 61.1, 60.3, 54.5, 47.3, 46.4, 45.9, 44.3, 41.5, 40.9, 40.7, 39.1, 37.3, 33.7, 33.1, 32.3, 30.6, 28.2, 27.4, 25.5, 23.6, 23.3, 22.8, 20.9, 17.9, 17.4, 16.8, 16.3.

4.2.15. 2-α,3-β-di-(2, 3, 4, 6-tetra-O-benzoyl-glucosyloxy)-maslinic acid (6b)

It was prepared as a white solid from 4b by using the method established for 6a (0.83 g, 88.2%). $[\alpha]_D^{25} = +53°$ (c = 0.1, $CDCl_3$); mp: 161–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.05 (m, 2H), 8.01–7.98 (m, 4H), 7.94–7.92 (m, 4H), 7.88–7.87 (m, 2H), 7.84–7.82 (m, 4H), 7.52–7.45 (m, 4H), 7.43–7.39 (m, 6H), 7.35–7.29 (m, 6H), 7.28–7.27 (m, 1H), 7.25–7.22 (m, 7H), 6.00–5.96 (m, 2H), 5.89–5.82 (m, 5H), 5.68–5.65 (m, 1H), 5.59–5.56 (m, 1H), 5.26–5.23 (m, 2H), 5.02 (d, 1H, *J* = 7.6 Hz), 4.93–4.90 (m, 1H), 4.75–4.70 (m, 2H), 4.63–4.60 (m, 1H), 4.47–4.44 (m, 1H), 4.27–4.24 (m, 1H), 4.15–4.11 (m, 1H), 3.15 (d, 1H, *J* = 9.2 Hz), 2.85–2.82 (m, 1H), 2.08–2.06 (m, 1H), 1.98–1.94 (m, 1H), 1.81–1.70 (m, 3H), 1.65–1.58 (m, 4H), 1.38–1.14 (m, 11H), 0.97 (s, 3H), 0.96 (s, 3H), 0.95 (s, 3H), 0.77 (s, 3H), 0.76 (s, 3H), 0.64 (s, 3H), 0.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.0, 166.1, 165.9, 165.8, 165.3, 165.1, 165.0, 143.6, 133.0, 132.9, 132.8, 132.7, 129.9, 129.8, 129.7, 129.6, 129.3, 129.1, 129.0, 128.3, 128.2, 128.1, 122.1, 101.6, 97.3, 89.2, 73.7, 73.6, 73.4, 73.2, 72.7, 72.4, 71.3, 70.8, 70.2, 64.2, 63.7, 54.5, 47.3, 46.5, 45.9, 43.0, 41.5, 40.8, 40.1, 39.1, 37.3, 33.7, 33.0, 32.3, 30.6, 29.6, 28.4, 27.5, 25.6, 23.6, 23.3, 22.9, 17.9, 17.7, 16.9, 16.2.

4.2.16. 2-α,3-β-di-(2, 3, 4-tri-O-benzoyl-arabinosyloxy)-maslinic acid (6c)

It was prepared as a white solid from 4c by using the method established for 6a (1.30 g, 88.4%). $[\alpha]_D^{25} = +112°$ (c = 0.1, $CDCl_3$); mp: 195–196 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.04 (m, 1H), 8.03–7.99 (m, 5H), 7.90–7.86 (m, 4H), 7.82–7.80 (m, 2H), 7.53–7.49 (m, 2H), 7.48–7.43 (m, 4H), 7.42–7.37 (m, 4H), 7.34–7.33 (m, 2H), 7.32–7.31 (m, 3H), 7.30–7.28 (m, 3H), 5.81–5.77 (m, 1H), 5.69–5.64 (m, 3H), 5.62–5.58 (m, 2H), 5.26–5.25 (m, 1H), 5.03 (d, 1H, *J* = 5.2 Hz), 4.86 (d, 1H, *J* = 7.6 Hz), 4.73–4.60 (m, 1H), 4.33–4.30 (m, 1H), 4.07–3.99 (m, 2H), 3.91–3.88 (m, 1H), 3.14 (d, 1H, *J* = 9.3 Hz), 2.86–2.82 (m, 1H), 2.10–2.06 (m, 1H), 1.98–1.87 (m, 2H), 1.85–1.73 (m, 2H), 1.70–1.64 (m, 2H), 1.61–1.56 (m, 3H), 1.44–1.42 (m, 1H), 1.39–1.32 (m, 2H), 1.27–1.21 (m, 4H), 1.20–1.15 (m, 3H), 0.98 (s, 3H), 0.96 (s, 3H), 0.91 (s, 3H), 0.87 (s, 3H), 0.82 (s, 3H), 0.66 (s, 3H), 0.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.9, 165.7, 165.6, 165.4, 165.3, 165.2, 143.6, 133.4, 133.3, 133.1, 132.9, 130.0, 129.8, 129.7, 129.6, 129.5, 129.4, 129.1, 128.9, 128.4, 128.3, 128.1, 128.0, 122.1, 101.0, 98.7, 90.1, 75.0, 71.4, 70.7, 70.4, 69.2, 67.6, 64.2, 61.6, 60.3, 54.6, 47.2, 46.4, 46.0, 44.1, 41.5, 40.9, 40.5, 39.1, 37.3, 33.7, 32.3, 30.6, 28.3, 27.4, 26.8, 25.5, 23.6, 23.3, 22.8, 17.9, 16.9, 16.2.

4.2.17. 2-α,3-β-di-(2, 3, 5-tri-O-benzoyl-ribosyloxy)-maslinic acid (6d)

It was prepared as a white solid from 4d by using the method established for 6a (1.1 g, 90.9%). $[\alpha]_D^{25} = -40°$ (c = 0.1, $CDCl_3$); mp: 184–186 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.03 (m, 4H), 8.01–7.99 (m, 3H), 7.98–7.97 (m, 3H), 7.81–7.79 (m, 2H), 7.57–7.53 (m, 2H), 7.51–7.45 (m, 4H), 7.43–7.38 (m, 2H), 7.31–7.29 (m, 3H), 7.28–7.27 (m, 4H), 7.25–7.23 (m, 3H), 6.19 (t, 1H, *J* = 3.8 Hz), 6.11–6.09 (m, 1H), 5.70–5.68 (m, 2H), 5.59–5.57 (m, 1H), 5.48–5.47 (m, 2H), 5.35–5.32 (m, 1H), 5.27–5.23 (m, 1H), 4.74 (d, 1H, *J* = 12.2 Hz), 4.63–4.59 (m, 1H), 4.25–4.20 (m, 1H), 4.14–4.10 (m, 1H), 4.03–3.97 (m, 1H), 3.45 (d, 1H, *J* = 9.6 Hz), 2.83–2.79 (m, 1H), 2.24–2.20 (m, 1H), 2.03–1.98 (m, 1H), 1.93–1.91 (m, 2H), 1.75–1.68 (m, 2H), 1.65–1.53 (m, 6H), 1.45–1.36 (m, 2H), 1.34–1.24 (m, 4H), 1.23–1.19 (m, 2H), 1.17 (s, 3H), 1.11 (s, 3H), 0.96 (s, 3H), 0.91 (s, 6H), 0.78 (s, 3H), 0.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.8, 166.1, 166.0, 165.5, 165.3, 165.0, 143.5, 133.2, 133.0, 132.8, 130.1, 130.0, 129.9, 129.8, 129.7, 129.6, 128.4, 128.3, 128.2, 128.1, 122.2, 101.0, 93.7, 89.6, 70.7, 69.5, 69.4, 68.6, 68.3, 68.1, 67.6, 66.2, 62.4, 61.7, 60.3, 55.0, 47.6, 46.5, 45.7, 42.2, 41.6, 40.9, 40.7, 39.2, 37.5, 33.8, 33.0, 32.5, 32.3, 30.6, 28.5, 27.5, 26.8, 25.7, 23.5, 23.4, 22.9, 18.1, 17.5, 17.0, 16.4.

4.2.18. 2-α,3-β-di-(2, 3, 4, 6, 2', 3', 4', 6'-octa-O-benzoyl-lactosyloxy)-maslinic acid (6e)

It was prepared as a white solid from 4e by using the method established for 6a (1.3 g, 97.7%). $[\alpha]_D^{25} = +37°$ (c = 0.1, $CDCl_3$); mp: 184–185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14–8.12 (m, 2H), 8.03–8.01 (m, 2H), 8.01–7.99 (m, 3H), 7.99–7.95 (m, 10H), 7.94–7.90 (m, 5H), 7.85–7.83 (m, 2H), 7.76–7.73 (m, 4H), 7.64–7.59 (m, 2H), 7.57–7.51 (m, 4H), 7.50–7.47 (m, 5H), 7.46–7.41 (m, 6H), 7.40–7.35 (m, 8H), 7.34–7.27 (m, 7H), 7.25–7.21 (m, 7H), 7.20–7.16 (m, 3H), 5.80–5.69 (m, 6H), 5.51–5.43 (m, 2H), 5.40–5.29 (m, 2H), 5.16–5.11 (m, 1H), 4.87 (d, 1H, *J* = 7.5 Hz), 4.80–4.65 (m, 5H), 4.60–4.53 (m, 1H), 4.50–4.43 (m, 1H), 4.26 (t, 1H, *J* = 9.3 Hz), 4.15–4.10 (m, 1H), 3.97–3.87 (m, 4H), 3.83–3.75 (m, 4H), 3.71–3.67 (m, 1H), 3.45–3.39 (m, 1H), 3.01 (d, 1H, *J* = 9.1 Hz), 2.82–2.78 (m, 1H), 2.05–2.03 (m, 1H), 1.96–1.86 (m, 2H), 1.78–1.65 (m, 2H), 1.83–1.57 (m, 4H), 1.49–1.32 (m, 2H), 1.31–1.20 (m, 4H), 1.19–1.00 (m, 5H), 0.97 (s, 3H), 0.95 (s, 3H), 0.90 (s, 3H), 0.72 (s, 3H), 0.66 (s, 3H), 0.57 (s, 3H), 0.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.0, 165.9, 165.8, 165.4, 165.2, 165.0, 164.9, 164.7, 143.3, 133.4, 133.3, 133.2, 133.1, 133.0, 132.9, 132.8, 130.1, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 122.2, 102.0, 100.9, 100.8, 96.4, 89.3, 76.0, 74.1, 73.6, 73.4, 73.2, 72.9, 72.7, 72.0, 71.8, 71.7, 71.1, 70.9, 69.9, 67.6, 67.5, 67.3, 63.1, 60.9, 60.7, 60.3, 54.4, 53.7, 47.2, 46.4, 45.9, 44.0, 41.5, 40.8, 40.2, 39.0, 37.1, 33.1, 32.3, 30.6, 28.2, 27.4, 26.9, 25.5, 23.6, 23.2, 22.9, 21.0, 17.8, 17.3, 16.8, 16.1.

4.2.19. 2-α,3-β-di-(2, 3, 4, 6, 2', 3', 4', 6'-octa-O-benzoyl-maltosyloxy)-maslinic acid (6f)

It was prepared as a white solid from 4f by using the method established for 6a (1.51 g, 93.8%). $[\alpha]_D^{25} = +51°$ (c = 0.1, $CDCl_3$); mp: 173–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23–8.21 (m, 2H), 8.16–8.14 (m, 2H), 8.05–8.00 (m, 4H), 7.88–7.83 (m, 4H), 7.81–7.77 (m, 2H), 7.77–7.68 (m, 10H), 7.66–7.62 (m, 2H), 7.56–7.49 (m, 2H), 7.49–7.35 (m, 20H), 7.35–7.28 (m, 8H), 7.24–7.18 (m, 9H), 7.16–7.07 (m, 5H), 6.14–6.05 (m, 2H), 5.79–5.63 (m, 5H), 5.55–5.49 (m, 1H), 5.44–5.40 (m, 1H), 5.31–5.21 (m, 4H), 5.06–4.95 (m, 4H), 4.90–4.85 (m, 1H), 4.70–4.56 (m, 4H), 4.49–4.40 (m, 2H), 4.31–4.24 (m, 3H), 4.18–4.11 (m, 2H), 4.00–3.88 (m, 1H), 3.06 (d, 1H, *J* = 8.8 Hz), 2.87–2.77 (m, 1H), 2.08–2.02 (m, 1H), 2.01–1.91 (m, 2H), 1.80–1.70 (m, 2H), 1.67–1.54 (m, 5H), 1.43–1.34 (m, 1H), 1.32–1.03 (m, 9H), 0.96 (s, 3H), 0.94 (s, 6H), 0.71 (s, 6H), 0.60 (s, 3H), 0.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.3, 166.2, 165.9, 165.6, 165.5, 165.2, 165.1, 165.0, 164.9, 143.5, 133.4, 133.3, 133.2, 133.1, 133.0, 132.9, 132.8, 130.1, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 122.8, 101.6, 97.3, 97.0, 96.1, 90.8, 75.8, 75.2, 75.1, 73.8, 73.5, 73.4, 73.1, 72.6, 72.5, 72.1, 71.0, 70.8, 70.2, 69.1, 68.8, 64.3, 62.6, 60.8, 60.6, 60.4, 54.5, 52.7, 47.4, 46.5, 41.6, 40.2, 39.1, 37.3, 33.8, 33.1, 32.4, 30.7, 28.6, 28.4, 27.6, 25.7, 23.7, 23.4, 23.0, 18.0, 17.5, 16.9, 16.2.

4.2.20. 2-α,3-β-di-(2, 3, 4-tri-O-benzoyl-xylosyloxy)-corosolic acid (7a)

It was prepared as a white solid from 5a by using the method established for 6a (0.99 g, 87.6%). $[\alpha]_D^{25} = -23°$ (c = 0.1, $CDCl_3$); mp: 185–187 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13–8.08 (m, 5H), 8.03–8.01 (m, 3H), 7.98–7.93 (m, 6H), 7.56–7.54 (m, 1H), 7.51–7.46 (m, 4H), 7.43–7.41 (m, 3H), 7.38–7.34 (m, 5H), 7.31–7.28 (m, 3H), 5.95 (t, 1H, *J* = 9.2 Hz), 5.80–5.75 (m, 1H), 5.48–5.42 (m, 4H), 5.24–5.18 (m, 1H), 5.07–4.99 (m, 2H), 4.91 (d, 1H, *J* = 6.7 Hz), 4.50–4.43 (m, 1H), 3.98–3.90 (m, 2H), 3.68 (t, 1H, *J* = 10.2 Hz), 3.18 (d, 1H, *J* = 9.1 Hz), 2.20 (d, 1H, *J* = 10.6 Hz), 2.06–1.94 (m, 3H), 1.92–1.81 (m, 2H), 1.74–1.60 (m, 5H), 1.53–1.50 (m, 1H), 1.42–1.41 (m, 1H), 1.35–1.16 (m, 8H), 0.96 (s, 3H), 0.91 (s, 12H), 0.69 (s, 3H), 0.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 165.8, 165.7, 165.3, 165.2, 164.9, 138.2, 133.2, 133.1, 133.0, 130.1, 130.0, 129.8, 129.7, 129.4, 129.3, 129.1, 129.0, 128.3, 128.2, 128.1, 128.0, 125.1, 100.8,

99.2, 89.0, 74.6, 72.5, 72.0, 70.2, 70.1, 69.7, 69.3, 63.1, 60.9, 60.3, 54.6, 52.4, 47.8, 47.2, 44.2, 41.7, 40.9, 39.3, 38.9, 38.7, 37.4, 36.6, 32.5, 30.5, 28.2, 27.8, 26.8, 23.9, 23.4, 23.2, 21.1, 20.9, 18.0, 17.3, 17.1, 16.9, 16.6.

4.2.21. 2-α,3-β-di-(2, 3, 4, 6-tetra-O-benzoyl-glucosyloxy)-corosolic acid (7b)

It was prepared as a white solid from 5b by using the method established for 6a (1.05 g, 85.0%). $[\alpha]_D^{25} = +63°$ (c = 0.1, $CDCl_3$); mp: 168–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.05 (m, 2H), 8.02–7.99 (m, 2H), 7.95–7.93 (m, 4H), 7.88–7.86 (m, 2H), 7.51–7.50 (m, 1H), 7.49–7.45 (m, 3H), 7.43–7.38 (m, 7H), 7.36–7.30 (m, 7H), 7.28–7.26 (m, 2H), 7.25–7.21 (m, 4H), 6.01–5.97 (m, 2H), 5.90–5.82 (m, 2H), 5.69–5.66 (m, 1H), 5.61–5.58 (m, 1H), 5.24–5.22 (m, 2H), 5.01(d, 1H, *J* = 7.5 Hz), 4.79–4.76 (m, 1H), 4.73–4.70 (m, 1H), 4.65–4.62 (m, 1H), 4.46–4.43 (m, 1H), 4.28–4.25 (m, 1H), 4.13–4.09 (m, 1H), 3.15 (d, 1H, *J* = 9.3 Hz), 2.21 (d, 1H, *J* = 11.2 Hz), 2.09–2.07 (m, 1H), 2.02–1.97 (m, 1H), 1.82–1.65 (m, 7H), 1.55–1.53 (m, 1H), 1.35–1.26 (m, 6H), 1.20–1.16 (m, 2H), 1.11–1.04 (m, 2H), 0.99 (d, 3H, *J* = 6.2 Hz), 0.95 (s, 3H), 0.93 (d, 3H, *J* = 6.4 Hz), 0.81 (s, 3H), 0.78 (s, 3H), 0.66 (s, 3H), 0.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.8, 166.1, 165.8, 165.3, 165.0, 138.0, 133.1, 133.0, 132.9, 132.8, 132.6, 129.9, 129.8, 129.7, 129.6, 129.2, 129.1, 129.0, 128.3, 128.2, 128.1, 128.0, 125.2, 101.6, 97.5, 88.9, 73.8, 73.6, 73.3, 73.2, 72.7, 72.3, 71.3, 70.9, 70.2, 64.2, 63.7, 54.5, 52.4, 47.9, 47.3, 43.1, 41.8, 40.2, 39.3, 39.0, 38.8, 37.2, 36.6, 32.5, 30.5, 29.6, 28.4, 27.8, 24.0, 23.4, 23.2, 21.1, 17.9, 17.6, 17.0, 16.8, 16.4.

4.2.22. 2-α,3-β-di-(2, 3, 4-tri-O-benzoyl-arabinosyloxy)-corosolic acid (7c)

It was prepared as a white solid from 5c by using the method established for 6a (1.25 g, 88.7%). $[\alpha]_D^{25} = +122°$ (c = 0.1, $CDCl_3$); mp: 198–199 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.03 (m, 1H), 8.02–7.97 (m, 5H), 7.86–7.80 (m, 4H), 7.75–7.74 (m, 2H), 7.52–7.45 (m, 3H), 7.43–7.39 (m, 4H), 7.38–7.34 (m, 3H), 7.33–7.27 (m, 5H), 7.25–7.22 (m, 3H), 5.77 (t, 1H, *J* = 8.8 Hz), 5.66–5.55 (m, 5H), 5.25–5.18 (m, 1H), 5.00 (d, 1H, *J* = 4.5 Hz), 4.85 (d, 1H, *J* = 7.6 Hz), 4.79–4.65 (m, 1H), 4.28 (d, 1H, *J* = 12.8 Hz), 4.07–3.97 (m, 2H), 3.89–3.85 (m, 1H), 3.13 (d, 1H, *J* = 9.4 Hz), 2.18 (d, 1H, *J* = 11.1 Hz), 2.09–2.06 (m, 1H), 2.01–1.89 (m, 2H), 1.86–1.58 (m, 6H), 1.51–1.49 (m, 1H), 1.40–1.37 (m, 1H), 1.33–1.08 (m, 7H), 0.96 (s, 3H), 0.89 (d, 9H, *J* = 7.4 Hz), 0.83 (s, 3H), 0.67 (s, 3H), 0.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.5, 166.1, 166.0, 165.5, 165.2, 164.9, 137.9, 133.2, 133.0, 132.8, 130.1, 129.9, 129.8, 129.7, 129.6, 128.4, 128.3, 128.2, 128.1, 125.3, 100.9, 93.7, 89.5, 70.6, 69.5, 69.3, 68.3, 68.0, 67.5, 66.2, 62.4, 61.6, 54.9, 52.4, 47.8, 47.4, 42.2, 41.9, 40.7, 39.4, 38.9, 38.7, 37.5, 36.6, 32.7, 30.5, 28.5, 27.9, 26.8, 23.9, 23.4, 23.3, 21.1, 18.1, 17.5, 17.0, 16.5.

4.2.23. 2-α,3-β-di-(2, 3, 5-tri-O-benzoyl-ribosyloxy)-corosolic acid (7d)

It was prepared as a white solid from 5d by using the method established for 6a (1.01 g, 89.4%). $[\alpha]_D^{25} = -52°$ (c = 0.1, $CDCl_3$); mp: 185–187 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.02 (m, 5H), 7.98–7.96 (m, 6H), 7.79–7.77 (m, 2H), 7.56–7.52 (m, 2H), 7.50–7.44 (m, 4H), 7.43–7.37 (m, 3H), 7.30–7.27 (m, 4H), 7.25–7.22 (m, 4H), 6.20–6.17 (m, 1H), 6.11–6.06 (m, 1H), 5.71–5.65 (m, 2H), 5.58–5.54 (m, 1H), 5.50–5.44 (m, 2H), 5.34–5.30 (m, 1H), 5.23–5.19 (m, 1H), 4.73 (d, 1H, *J* = 12.3 Hz), 4.63–4.56 (m, 1H), 4.23–4.19 (m, 1H), 4.12–4.09 (m, 1H), 4.02–3.95 (m, 1H), 3.44 (d, 1H, *J* = 9.4 Hz), 2.24–2.22 (m, 1H), 2.18–2.15 (m, 1H), 2.02–1.90 (m, 4H), 1.86–1.80 (m, 1H), 1.70–1.59 (m, 4H), 1.55–1.41 (m, 5H), 1.34–1.23 (m, 5H), 1.16 (s, 3H), 1.05 (s, 3H), 0.95 (s, 3H), 0.96 (s, 3H), 0.85 (s, 3H), 0.76 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.5, 166.1, 165.5, 165.3, 164.9, 137.9, 132.2, 133.0, 132.9, 132.8, 130.1, 130.0, 129.9, 129.8, 129.7, 129.6, 128.4, 128.3, 128.2, 128.1, 125.3, 101.0, 93.7, 89.5, 70.7, 69.5, 69.3, 68.1, 67.5, 66.2, 62.4, 61.7, 55.0, 52.4, 47.9, 47.5, 42.3, 41.9, 40.7, 39.5, 39.0, 38.7, 37.5, 36.6, 32.8, 30.5, 28.8, 27.9, 26.8, 24.0, 23.4, 23.3, 21.1, 18.1, 17.5, 17.0, 16.5.

4.2.24. 2-α,3-β-di-(2, 3, 4, 6, 2', 3', 4', 6'-octa-O-benzoyl-lactosyloxy)-corosolic acid (7e)

It was prepared as a white solid from 5e by using the method established for 6a (2.13 g, 91.8%). $[\alpha]_D^{25} = +47°$ (c = 0.1, $CDCl_3$); mp: 183–185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13–8.11 (m, 2H), 8.05–8.03 (m, 2H), 8.01–7.98 (m, 6H), 7.97–7.96 (m, 4H), 7.95–7.92 (m, 4H), 7.91–7.88 (m, 3H), 7.83–7.82 (m, 2H), 7.76–7.73 (m, 4H), 7.64–7.58 (m, 2H), 7.57–7.53 (m, 2H), 7.52–7.43 (m, 13H), 7.41–7.28 (m, 16H), 7.25–7.16 (m, 10H), 5.81–5.69 (m, 6H), 5.51–5.42 (m, 2H), 5.39–5.31 (m, 2H), 5.15–5.10 (m, 1H), 4.85 (d, 1H, *J* = 7.4 Hz), 4.79–4.71 (m, 4H), 4.63–4.60 (m, 1H), 4.53–4.48 (m, 1H), 4.24 (t, 1H, *J* = 9.2 Hz), 4.15–4.08 (m, 1H), 3.98–3.93(m, 1H), 3.91–3.80 (m, 4H), 3.79–3.71 (m, 3H), 3.68–3.62 (m, 1H), 3.44–3.38 (m, 1H), 3.01 (d, 1H, *J* = 9.0 Hz), 2.17 (d, 1H, *J* = 11.0 Hz), 2.04–1.87 (m, 4H), 1.75–1.61 (m, 5H), 1.55–1.50 (m, 2H), 1.44–1.42 (m, 1H), 1.36–1.20 (m, 6H), 1.18–1.13 (m, 2H), 0.98 (s, 3H), 0.88 (s, 6H), 0.73 (s, 3H), 0.69 (s, 3H), 0.59 (s, 3H), 0.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.0, 165.8, 165.4, 165.3, 165.2, 165.0, 164.9, 164.6, 137.9, 133.4, 133.2, 133.1, 133.0, 132.8, 130.1, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 125.3, 102.0, 100.9, 100.7, 96.8, 89.1, 76.1, 74.4, 73.6, 73.4, 73.2, 72.8, 71.9, 71.8, 71.7, 71.1, 70.8, 69.9, 67.4, 67.2, 63.1, 60.7, 60.3, 60.2, 54.5, 52.4, 47.8, 47.3, 44.2, 41.8, 40.4, 39.3, 39.0, 38.8, 37.2, 36.6, 32.5, 30.6, 28.2, 27.8, 26.9, 23.3, 23.0, 21.1, 21.0, 17.9, 17.2, 17.1, 16.7, 16.3.

4.2.25. 2-α,3-β-di-(2, 3, 4, 6, 2', 3', 4', 6'-octa-O-benzoyl-maltosyloxy)-corosolic acid (7f)

It was prepared as a white solid from 5f by using the method established for 6a (1.84 g, 98.9%). $[\alpha]_D^{25} = +48°$ (c = 0.1, $CDCl_3$); mp: 173–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24–8.22 (m, 2H), 8.18–8.16 (m, 2H), 8.07–8.02 (m, 4H), 7.90–7.85 (m, 4H), 7.81–7.79 (m, 2H), 7.75–7.70 (m, 10H), 7.62–7.60 (m, 2H), 7.55–7.51 (m, 2H), 7.50–7.44 (m, 7H), 7.43–7.37 (m, 13H), 7.36–7.27 (m, 9H), 7.24–7.17 (m, 9H), 7.16–7.09 (m, 4H), 6.15–6.06 (m, 2H), 5.82–5.75 (m, 2H), 5.74–5.64 (m, 3H), 5.53–5.49 (m, 1H), 5.43 (t, 1H, *J* = 4.1 Hz), 5.32–5.25 (m, 3H), 5.23–5.18 (m, 1H), 5.07–4.94 (m, 4H), 4.87 (d, 1H, *J* = 7.5 Hz), 4.73–4.69 (m, 1H), 4.62–4.53 (m, 3H), 4.50–4.46 (m, 1H), 4.45–4.39 (m, 1H), 4.35–4.30 (m, 2H), 4.27–4.22 (m, 1H), 4.18–4.10 (m, 2H), 3.95–3.93 (m, 1H), 3.06 (d, 1H, *J* = 9.2 Hz), 2.20 (d, 1H, *J* = 10.9 Hz), 2.05–1.94 (m, 3H), 1.81–1.64 (m, 6H), 1.55–1.52 (m, 1H), 1.44–1.24 (m, 7H), 1.19–1.05 (m, 3H), 0.99 (s, 3H), 0.92 (s, 6H), 0.76 (s, 3H), 0.74 (s, 3H), 0.65 (s, 3H), 0.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.4, 166.2, 166.1, 165.8, 165.7, 165.5, 165.4, 165.1, 165.0, 164.9, 164.8, 137.9, 133.4, 133.2, 133.1, 132.9, 132.8, 132.7, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.0, 128.9, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 125.5, 101.5, 97.4, 96.9, 96.1, 88.9, 75.2, 74.9, 73.9, 73.5, 73.4, 73.3, 72.5, 72.4, 70.9, 70.7, 70.1, 69.1, 68.7, 64.2, 62.5, 62.4, 54.4, 52.4, 47.8, 47.3, 43.5, 41.8, 40.2, 39.3, 39.0, 38.8, 37.2, 36.6, 32.5, 30.5, 28.3, 27.8, 26.8, 24.0, 23.4, 21.1, 18.0, 17.4, 17.0, 16.8, 16.3.

4.2.26. 2-α,3-β-di-xylosyloxy-maslinic acid (8a)

Sodium methoxide–methanol solution (33%, 1.1 mL) was added dropwise to a suspension of 6a (920 mg, 0.676 mmol) in MeOH (20 mL) at room temperature and the mixture was stirred for 5 h. The reaction was neutralized with Dowex H^+ resin to pH 7, filtered and then concentrated in vacuo. The residue was purified by silica-gel column chromatography (9:1, $CHCl_3$-MeOH) to give 8a as white solid (498 mg, 88.3%). $[\alpha]_D^{25} = -35°$ (c = 0.1, DMSO); mp: 253–255 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.14 (s, 1H), 4.46 (d, 1H, *J* = 4.4 Hz), 4.30 (d, 1H, *J* = 7.1 Hz), 4.02–4.01 (m, 1H), 3.71–3.68 (m, 1H), 3.65–3.62 (m, 2H), 3.54–3.36 (m, 8H), 3.32–3.30 (m, 2H), 3.28–3.26 (m, 1H), 3.23–3.13 (m, 5H), 3.09–3.06 (m, 1H), 3.05–3.02 (m,

1H), 2.99–2.95 (m, 1H), 2.74–2.72 (m, 1H), 1.97–1.96 (m, 1H), 1.89–1.82 (m, 3H), 1.86–1.56 (m, 3H), 1.52–1.45 (m, 3H), 1.42–1.36 (m, 2H), 1.31–1.26 (m, 2H), 1.23–1.21 (m, 1H), 1.07 (s, 3H), 1.02 (s, 3H), 0.87 (s, 3H), 0.86 (s, 3H), 0.85 (s, 3H), 0.79 (s, 3H), 0.69 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.8, 144.1, 121.3, 104.4, 96.4, 86.5, 76.5, 73.7, 72.1, 70.5, 70.1, 69.5, 69.3, 65.4, 62.8, 54.3, 52.2, 47.1, 45.8, 45.5, 44.0, 41.4, 40.9, 38.9, 37.3, 33.5, 32.9, 32.4, 32.2, 30.5, 28.1, 25.7, 23.5, 23.2, 22.7, 17.8, 17.7, 16.9, 16.3. HRMS (ESI): Calcd for $C_{40}H_{64}O_{12}Na$ $[M+Na]^+$: 759.4290; found:759.4259.

4.2.27. 2-α,3-β-di-glucosyloxy-maslinic acid (8b)

It was prepared as a white solid from 6b by using the method established above for 8a (320 mg, 86.7%). $[\alpha]_D^{25}$ = +29° (c = 0.1, DMSO); mp: 232–233 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.15 (s, 1H), 4.95–4.83 (m, 3H), 4.80–4.70 (m, 2H), 4.39–4.38 (m, 1H), 4.28 (d, 1H, *J* = 7.6 Hz), 4.10–4.03 (m, 1H), 3.89–3.85 (m, 1H), 3.66 (d, 2H, *J* = 10.7 Hz), 3.45–3.33 (m, 10H), 3.21 (d, 1H, *J* = 9.5 Hz), 3.14–3.01 (m, 7H), 2.74–2.71 (m, 1H), 2.07 (d, 1H, *J* = 9.1 Hz), 1.91–1.83 (m, 3H), 1.65–1.57 (m, 3H), 1.52–1.45 (m, 3H), 1.43–1.38 (m, 2H), 1.32–1.28 (m, 2H), 1.23–1.22 (m, 1H), 1.08 (s, 3H), 1.05 (s, 3H), 0.87 (s, 3H), 0.86 (s, 6H), 0.77 (s, 3H), 0.69 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.6, 144.0, 121.3, 103.6, 96.9, 86.9, 77.1, 76.9, 76.6, 76.5, 74.2, 72.9, 71.1, 70.1, 61.5, 61.2, 54.7, 52.1, 47.1, 45.7, 45.5, 43.8, 41.4, 40.9, 40.3, 38.9, 37.1, 33.4, 32.9, 32.4, 32.1, 30.4, 28.5, 27.2, 25.8, 23.4, 23.1, 22.7, 18.0, 16.8, 16.1. HRMS (ESI): Calcd for $C_{42}H_{68}O_{14}Na$ $[M+Na]^+$: 819.4501; found: 819.4464.

4.2.28. 2-α,3-β-di-arabinosyloxy-maslinic acid (8c)

It was prepared as a white solid from 6c by using the method established for 8a (497 mg, 80.6%). $[\alpha]_D^{25}$ = –27° (c = 0.1, DMSO); mp: 266–268 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.14 (s, 1H), 5.10–5.02 (m, 1H), 4.88 (s, 1H), 4.50 (s, 1H), 4.28 (d, 1H, *J* = 7.1 Hz), 4.16 (d, 1H, *J* = 12.2 Hz), 4.04 (t, 1H, *J* = 11.0 Hz), 3.92 (d, 1H, *J* = 10.9 Hz), 3.76–3.74 (m, 1H), 3.69–3.65 (m, 1H), 3.61–3.59 (m, 1H), 3.52–3.49 (m, 1H), 3.40–3.34 (m, 11H), 3.29–3.27 (m, 1H), 3.25–3.22 (m, 1H), 3.15 (d, 1H, *J* = 9.8 Hz), 2.74–2.72 (m, 1H), 1.91–1.88 (m, 2H), 1.84–1.83 (m, 2H), 1.66–1.53 (m, 4H), 1.51–1.36 (m, 4H), 1.33–1.26 (m, 2H), 1.24–1.22 (m, 1H), 1.06 (s, 3H), 1.02 (s, 3H), 0.88 (s, 3H), 0.86 (s, 6H), 0.82 (s, 3H), 0.69 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.7, 144.0, 121.3, 104.2, 96.2, 85.9, 72.9, 71.2, 70.7, 70.0, 68.0, 64.9, 63.5, 59.1, 54.0, 47.0, 45.7, 45.5, 43.6, 41.4, 41.1, 40.8, 38.9, 37.2, 33.4, 32.8, 32.3, 32.1, 30.4, 28.1, 27.2, 25.6, 23.5, 23.1, 22.6, 17.7, 16.8, 16.3. HRMS (ESI): Calcd for $C_{40}H_{64}O_{12}Na$ $[M+Na]^+$: 759.4290; found: 759.4257.

4.2.29. 2-α,3-β-di-ribosyloxy-maslinic acid (8d)

It was prepared as a white solid from 6d by using the method established for 8a (420 mg, 88.2%). $[\alpha]_D^{25}$ = –54° (c = 0.1, DMSO); mp: 238–241 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.15 (s, 1H), 4.88–4.77 (m, 4H), 4.70–4.68 (m, 1H), 4.64 (d, 1H, *J* = 5.1 Hz), 4.06 (d, 1H, *J* = 10.4 Hz), 3.82–3.80 (m, 1H), 3.72–3.69 (m, 2H), 3.65–3.63 (m, 1H), 3.55–3.52 (m, 1H), 3.50–3.48 (m, 1H), 3.41–3.32 (m, 10H), 3.07 (d, 1H, *J* = 9.7 Hz), 2.74–2.72 (m, 1H), 1.99–1.98 (m, 1H), 1.91–1.84 (m, 3H), 1.65–1.53 (m, 3H), 1.53–1.41 (m, 5H), 1.32–1.22 (m, 4H), 1.08 (s, 3H), 0.98 (s, 3H), 0.88 (s, 3H), 0.86 (s, 6H), 0.76 (s, 3H), 0.69 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.6, 143.9, 121.4, 102.5, 96.4, 87.3, 71.4, 71.0, 69.9, 69.6, 68.5, 68.3, 65.6, 63.9, 63.7, 54.2, 52.1, 47.0, 45.7, 45.0, 42.7, 41.4, 40.8, 40.6, 38.9, 37.1, 33.4, 32.9, 32.3, 32.1, 30.4, 28.4, 27.2, 25.6, 23.4, 23.1, 22.6, 17.9, 17.7, 16.8, 16.2. HRMS (ESI): Calcd for $C_{40}H_{64}O_{12}Na$ $[M+Na]^+$: 759.4290; found: 759.4265.

4.2.30. 2-α,3-β-di-lactosyloxy-maslinic acid (8e)

It was prepared as a white solid from 6e by using the method established for 8a (390 mg, 70.9%). $[\alpha]_D^{25}$ = +34° (c = 0.1, DMSO); mp: 301–303 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.12 (s, 1H), 4.50–4.45 (m, 1H), 4.37–4.35 (m, 1H), 4.20–4.15 (m, 2H), 3.90–3.85 (m, 3H), 3.76–3.70 (m, 4H), 3.60–3.58 (m, 8H), 3.51–3.46 (m, 9H). 3.35–3.20 (m, 14H), 3.13–3.09 (m, 2H), 2.80–2.70 (m, 1H), 2.07–2.05 (m, 1H), 1.83–1.67 (m, 8H), 1.56–1.39 (m, 8H), 1.29–1.22 (m, 3H), 1.06 (s, 3H), 1.05 (s, 3H), 0.95 (s, 9H), 0.76 (s, 3H), 0.70 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 175.3, 144.6, 120.9, 104.0, 103.2, 98.7, 87.0, 81.3, 80.8, 75.6, 75.2, 74.9, 74.8, 74.0, 73.3, 72.7, 71.6, 70.7, 70.6, 68.2, 60.8, 60.7, 60.5, 54.8, 47.2, 46.1, 45.6, 43.8, 41.5, 41.1, 40.3, 38.9, 37.1, 33.7, 33.0, 32.5, 32.4, 30.5, 28.8, 27.3, 25.6, 23.6, 23.2, 22.9, 18.0, 17.1, 16.1. HRMS (ESI): Calcd for $C_{54}H_{88}O_{24}Na$ $[M+Na]^+$: 1143.5558; found: 1143.5514.

4.2.31. 2-α,3-β-di-maltosyloxy-maslinic acid (8f)

It was prepared as a white solid from 6f by using the method established for 8a (530 mg, 80.2%). $[\alpha]_D^{25}$ = +80° (c = 0.1, DMSO); mp: 280–282 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.13 (s, 1H), 5.00–4.95 (m, 2H), 4.44 (d. 1H, *J* = 7.1 Hz, 1H), 4.34 (d, 1H, *J* = 6.9 Hz, 1H), 3.92–3.88 (m, 1H), 3.71–3.66 (m, 2H), 3.61–3.59 (m, 3H), 3.55–3.50 (m, 5H), 3.48–3.42 (m, 9H), 3.40–3.34 (m, 7H), 3.31–3.21 (m, 10H), 3.12–3.02 (m, 6H), 2.76–2.73 (m, 1H), 2.12–2.05 (m, 1H), 1.90–1.80 (m, 3H), 1.66–1.39 (m, 9H), 1.30–1.20 (m, 4H), 1.07 (s, 3H), 1.05 (s, 3H), 0.87 (s, 3H), 0.86 (s, 6H), 0.76 (s, 3H), 0.70 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 176.5, 144.4, 121.0, 103.6, 100.9, 96.4, 87.3, 79.9, 79.7, 76.7, 76.2, 75.4, 75.0, 74.0, 73.5, 73.3, 72.8, 72.5, 71.3, 70.0, 69.9, 61.1, 60.9, 60.8, 60.7, 54.8, 47.2, 45.9, 45.6, 43.4, 41.5, 41.0, 40.3, 38.9, 37.1, 33.6, 33.0, 32.5, 32.3, 30.5, 28.6, 27.3, 25.6, 23.5, 23.2, 22.8, 18.0, 17.0, 16.1. HRMS (ESI): Calcd for $C_{54}H_{88}O_{24}Na$ $[M+Na]^+$: 1143.5558; found: 1143.5505.

4.2.32. 2-α,3-β-di-xylosyloxy-corosolic acid (9a)

It was prepared as a white solid from 7a by using the method established for 8a (400 mg, 86%). $[\alpha]_D^{25}$ = –42° (c = 0.1, DMSO); mp: 241–243 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.12 (s, 1H), 5.00–4.95 (m, 2H), 4.48 (d, 1H, *J* = 4.3 Hz), 4.31 (d, 1H, *J* = 7.1 Hz), 4.03–4.01 (m, 1H), 3.72–3.68 (m, 1H), 3.65–3.62 (m, 1H), 3.40–3.34 (m, 6H), 3.32–3.30 (m, 1H), 3.28–3.26 (m, 1H), 3.23–3.15 (m, 5H), 3.09–3.04 (m, 2H), 2.99–2.95 (m, 1H), 2.09 (d, 1H, *J* = 11.8 Hz), 2.03–2.01 (m, 1H), 1.91–1.85 (m, 3H), 1.80–1.76 (m, 1H), 1.58–1.56 (m, 1H), 1.52–1.48 (m, 4H), 1.43–1.41 (m, 2H), 1.29–1.23 (m, 5H), 1.02 (s, 6H), 0.90 (s, 3H), 0.89 (s, 3H), 0.80 (s, 3H), 0.79 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.3, 138.3, 124.4, 104.3, 96.2, 86.4, 76.4, 73.7, 72.0, 70.6, 70.2, 69.5, 69.3, 65.4, 62.7, 54.2, 52.4, 52.1, 47.0, 46.9, 44.0, 41.7, 40.8, 39.1, 38.5, 37.1, 36.3, 32.6, 30.2, 28.1, 27.5, 23.8, 23.2, 23.1, 21.1, 17.7, 17.0, 16.9, 16.4. HRMS (ESI): Calcd for $C_{40}H_{64}O_{12}Na$ $[M+Na]^+$: 759.4290; found: 759.4263.

4.2.33. 2-α,3-β-di-glucosyloxy-corosolic acid (9b)

It was prepared as a white solid from 7b by using the method established for 8a (450 mg, 94.7%). $[\alpha]_D^{25}$ = +35° (c = 0.1, DMSO); mp: 236–238 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.13 (s, 1H), 4.89–4.72 (m, 5H), 4.39–4.37 (m, 2H), 4.29 (d, 1H, *J* = 7.5 Hz), 4.10–4.00 (m, 1H), 3.91–3.87 (m, 1H), 3.66 (d, 2H, *J* = 10.6 Hz), 3.45–3.30 (m, 8H), 3.20 (d, 1H, *J* = 9.5 Hz), 3.15–2.99 (m, 8H), 2.13–2.09 (m, 2H), 1.92–1.76 (m, 4H), 1.57–1.41 (m, 6H), 1.28–1.26 (m, 4H), 1.05 (s, 3H), 1.02 (s, 3H), 0.89 (s, 3H), 0.88 (s, 3H), 0.79 (s, 3H), 0.77 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.3, 138.3, 124.4, 103.6, 98.7, 87.1, 77.2, 76.9, 76.6, 74.3, 73.0, 70.9, 70.2, 70.1, 61.6, 61.3, 54.7, 52.5, 52.1, 47.0, 46.9, 43.8, 41.8, 40.3, 38.5, 37.0, 36.3, 32.7, 30.2, 28.6, 27.5, 23.8, 23.2, 23.1, 21.1, 18.0, 17.0, 16.9, 16.2. HRMS (ESI): Calcd for $C_{42}H_{68}O_{14}Na$ $[M+Na]^+$: 819.4501; found: 819.4465.

4.2.34. 2-α,3-β-di-arabinosyloxy-corosolic acid (9c)

It was prepared as a white solid from 7c by using the method established for 8a (500 mg, 88.0%). $[\alpha]_D^{25}$ = –25° (c = 0.1, DMSO); mp: 257–260 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.11 (s, 1H), 4.51 (s, 1H), 4.28 (d, 1H, *J* = 7.0 Hz), 4.03 (t, 1H, *J* = 10.9 Hz), 3.96–3.89 (m, 1H), 3.75 (d, 1H, *J* = 10.7 Hz), 3.69–3.63 (m, 2H), 3.60–3.58 (m, 3H), 3.54–3.49 (m, 2H), 3.47–3.44 (m, 2H), 3.40–3.36 (m, 2H), 3.34–3.28 (m, 4H), 3.25–3.22 (m, 1H), 3.16 (d, 1H, *J* = 9.8 Hz), 2.10 (d, 1H,

J = 11.2 Hz), 1.95–1.94 (m, 1H), 1.90–1.86 (m, 3H), 1.83–1.79 (m, 1H), 1.57–1.48(m, 6H),1.43–1.41 (m, 2H), 1.30–1.22 (m, 5H), 1.02 (s, 6H), 0.90 (s, 6H), 0.82 (s, 3H), 0.80 (d, 3H, *J* = 6.2 Hz), 0.72 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.6, 138.4, 124.3, 104.2, 96.2, 85.9, 72.9, 71.3, 70.7, 70.6, 70.0, 68.0, 64.9, 63.5, 59.1, 54.0, 52.5, 52.1, 47.0, 46.9, 43.7, 41.8, 41.1, 39.1, 38.6, 38.5, 37.1, 36.4, 32.6, 30.3, 28.1, 27.6, 23.9, 23.2, 23.1, 21.1, 17.7, 17.1, 17.0, 16.4. HRMS (ESI): Calcd for $C_{40}H_{64}O_{12}Na$ $[M + Na]^+$: 759.4290; found: 759.4258.

4.2.35. 2-α,3-β-di-ribosyloxy-corosolic acid (9d)

It was prepared as a white solid from 7d by using the method established for 8a (440 mg, 75.3%). $[\alpha]_D^{25} = -75°$ (c = 0.1, DMSO); mp: 235–238 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.12 (s, 1H), 4.88–4.83 (m, 1H), 4.80–4.74 (m, 3H), 4.73–4.69 (m, 2H), 4.65 (d, 1H, *J* = 5.0 Hz), 4.05 (d, 1H, *J* = 10.5 Hz), 3.82–3.79 (m, 1H), 3.73–3.69 (m, 2H), 3.67–3.63 (m, 1H), 3.53–3.49 (m, 2H), 3.40–3.32 (m, 10H), 3.07 (d, 1H, *J* = 9.6 Hz), 2.09 (d, 1H, *J* = 11.2 Hz), 2.05–2.02 (m, 1H), 1.93–1.88 (m, 2H), 1.80–1.76 (m, 1H), 1.58–1.56 (m, 1H), 1.52–1.48 (m, 4H), 1.43–1.41 (m, 2H), 1.28–1.24 (m, 4H),1.03 (s, 3H), 0.98 (s, 3H), 0.90 (s, 3H), 0.89 (s, 3H), 0.80 (d, 3H, *J* = 6.4 Hz), 0.76 (s, 3H), 0.73 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.3, 138.3, 124.4, 102.5, 96.3, 87.4, 71.4, 71.0, 69.9, 69.6, 68.5, 68.1, 65.7, 63.9, 63.7, 54.1, 52.4, 52.1, 46.9, 42.8, 41.7, 40.6, 39.1, 38.5, 38.4, 37.0, 36.3, 32.6, 30.2, 28.5, 27.5, 23.8, 23.2, 23.0, 21.1, 17.8, 17.0, 16.9, 16.3. HRMS (ESI): Calcd for $C_{40}H_{64}O_{12}Na$ $[M + Na]^+$: 759.4290; found: 759.4257.

4.2.36. 2-α,3-β-di-lactosyloxy-corosolic acid (9e)

It was prepared as a white solid from 7e by using the method established for 8a (510 mg, 70.2%). $[\alpha]_D^{25} = +26°$ (c = 0.1, DMSO); mp: 291–293 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.10 (s, 1H), 4.47 (d, 1H, *J* = 7.5 Hz), 4.36 (d, 1H, *J* = 7.0 Hz), 4.18–4.15 (m, 2H), 3.90–3.88 (m, 1H), 3.76–3.74 (m, 2H), 3.62–3.59 (m, 4H), 3.58–3.54 (m, 4H), 3.53–3.50 (m, 4H), 3.49–3.42 (m, 8H), 3.33–3.28 (m, 9H), 3.27–3.21 (m, 6H), 3.12–3.06 (m, 2H), 2.13–2.12 (m, 2H), 1.91–1.83 (m, 4H), 1.73 (s, 2H), 1.55–1.39 (m, 8H), 1.26–1.21 (m, 5H), 1.05 (s, 3H), 1.01 (s, 3H), 0.88 (s, 6H), 0.79 (s, 3H), 0.76 (s, 3H), 0.74 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 176.2, 138.8, 124.0, 104.1, 103.3, 98.3, 87.2, 81.4, 80.9, 79.2, 75.6, 75.2, 75.0, 74.8, 74.7, 74.1, 73.3, 72.8, 71.5, 70.7, 70.6, 68.2, 60.9, 60.8, 60.5, 54.8, 52.7, 47.1, 47.0, 43.7, 41.8, 40.2, 38.7, 37.0, 36.6, 32.8, 30.5, 28.7, 27.7, 24.1, 23.7, 23.2, 23.1, 21.3, 18.1, 18.0, 17.2, 16.3. HRMS (ESI): Calcd for $C_{54}H_{88}O_{24}Na$ $[M + Na]^+$: 1143.5558; found: 1143.5508.

4.2.37. 2-α,3-β-di-maltosyloxy-corosolic acid (9f)

It was prepared as a white solid from 7f by using the method established for 8a (540 mg, 74.4%). $[\alpha]_D^{25} = +41°$ (c = 0.1, DMSO); mp: 280–283 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.10 (s, 1H), 4.99–4.95 (m, 2H), 4.44 (d, 1H, *J* = 7.4 Hz), 4.35 (d, 1H, *J* = 7.3 Hz), 3.93–3.89 (m, 1H), 3.70 (t, 3H, *J* = 11.8 Hz), 3.61–3.59 (m, 4H), 3.56–3.49 (m, 4H), 3.46–3.43 (m, 6H), 3.42–3.34 (m, 6H), 3.30–3.27 (m, 2H), 3.26–3.20 (m, 8H), 3.11–3.02 (m, 6H), 2.12 (d, 2H, *J* = 10.1 Hz), 1.92–1.83 (m, 4H), 1.74 (s, 2H), 1.55–1.39 (m, 8H), 1.26–1.21 (m, 5H), 1.05 (s, 3H), 1.01 (s, 3H), 0.89 (s, 3H), 0.88 (s, 3H), 0.79 (s, 3H), 0.76 (s, 3H), 0.73 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 175.5, 138.7, 124.1, 103.6, 100.9, 98.2, 87.6, 80.0, 79.8, 79.2, 76.7, 76.3, 75.5, 75.0, 74.0, 73.5, 73.3, 72.7, 72.5, 71.2, 70.1, 70.0, 61.1, 60.9, 60.7, 54.8, 52.7, 47.1, 47.0, 43.4, 41.8, 40.3, 38.7, 37.0, 36.5, 32.8, 30.5, 28.6, 27.7, 24.0, 23.5, 23.2, 23.1, 21.2, 18.1, 18.0, 17.2, 16.2. HRMS (ESI): Calcd for $C_{54}H_{88}O_{24}Na$ $[M + Na]^+$: 1143.5558; found: 1143.5501.

4.3. Enzyme inhibition assay

4.3.1. α-Glucosidase inhibition assay

The α-glucosidase inhibition assay was performed according to a reported method with modifications.[37,38] The reaction system contained 67 mM KH_2PO_4-K_2HPO_4 (pH 6.8), 1 U/mL α- glucosidase and 5.8 mM 4-nitrophenyl-α-D-glucopyranoside (PNPG). Solution of the inhibitors, i.e., glycosylated derivatives of dihydroxylpentacyclic triterpene acids and acarbose (positive control), were prepared with ethanol–water (1:1) at a series of concentrations. The reaction mixture was pre-incubated at 37 °C for 15 minutes after addition of KH_2PO_4-K_2HPO_4 buffer, 10 μL α-glucosidase and a certain volume of inhibitor. A 20 μL aliquot of PNPG solution was then added to the reaction mixture in a final volume of 250 μL, which was further incubated at 37 °C for 10 minutes, and the absorbance was recorded by microplate reader at 405 nm. The percentage of inhibition was calculated using $[(A-(A_1-A_2))/A] \times 100\%$, where A was the absorbance without the derivative, A_1 was the absorbance with the derivative and A_2 was background reference of derivative. Each experiment was carried out in four replicates at least. The IC_{50} value was determined from a plot of the percentage of inhibition versus the sample concentration. Acarbose was used as a positive control and was evaluated under the same procedure. In addition, to further analyze the inhibitory activity of α-glucosidase of the parent compounds (low water solubility) and their derivatives under the identical conditions and the structure-activity relationship, DMSO was also used as the solvent to perform the bioactivity assay. The method was described above for α-glucosidase inhibition assay (ethanol–water system).

4.3.2. Measurement of kinetic constants

For kinetic studies of α-glucosidase inhibition by the synthesized glycosides (i.e., 9e), enzyme and inhibitor at various concentrations (0, 0.821, 1.642, 2.463 mM) were incubated with increasing concentrations of substrate PNPG (0.232, 0.348, 0.464, 0.580, 0.696, 0.812, 0.928 mM). The enzyme activities were measured, and the kinetic constants and modes of inhibition for active compound were determined based on Lineweaver–Burk plots.[39]

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Appendix: Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.carres.2016.02.009.

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