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PENTACYCLIC TRITERPENOIDS FROM *RUBUS XANTHOCARPUS*

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Key Word Index—*Rubus xanthocarpus*; Rosaceae; pentacyclic triterpenoid; ursane; glucosyl ester.

Abstract—Eight pentacyclic triterpenoids have been isolated from the aerial parts of *Rubus xanthocarpus* and four of them are new compounds. Their structures were elucidated on the basis of spectral data and chemical transformations as: 1α,2α,3β,19α-tetrahydroxyurs-12-en-28-oic and, 2α,3α,19α,24-tetrahydroxyurs-12-en-28-oic acid-28-*O*-β-D-glucopyranusyl ester, 2α,3α,19α-trihydroxyurs-12-en-24-formyl-28-oic acid-28-*O*-β-D-glucopyranosyl ester and 2,3-*O*-isopropylidenyl-2α,3α,19α-trihydroxyurs-12-en-28-oic acid.

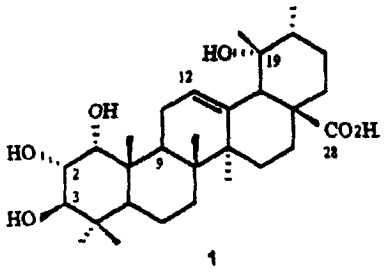
INTRODUCTION

Rubus xanthocarpus grows widely in the Northern regions of China [1]. The fruits, seeds, roots and leaves of this plant have been used as folk medicine for their anti-cancer and anti-bacterial activities for a long time in China [2]. Previous chemical investigations of this genus showed that ursane and oleanane triterpenoid saponins are the main components [3–6]. However, no chemical study of the species of *Rubus xanthocarpus* has been reported previously. Here we report the isolation and structural elucidation of four new compounds, 1α,2α,3β,19α-tetrahydroxyurs-12-en-28-oic acid (**1**), 2α,3α,19α,24-tetrahydroxyurs-12-en-28-oic acid-28-*O*-β-D-glucopyranosyl ester (**2**), 2α,3α,19α-trihydroxyurs-12-en-24-formyl-28-oic acid-28-*O*-β-D-glucopyranosyl ester (**3**), 2, 3-*O*-isopropylidenyl-2α,3α,19α-trihydroxyurs-12-en-28-oic acid (**4**), and of four known compounds (**5**–**8**) from this species.

RESULTS AND DISCUSSION

The *n*-butanol soluble part of the methanol extract from the aerial parts of *R. xanthocarpus* was rechromatographed over silica gel to afford compounds **2**, **3**, **4** and **6**. Compounds were treated with diazomethane and subjected to CC to give compounds **1a**, **5a**, **7a** and **8a**.

The known compounds were characterized as methyl 2α,3α,19α,23-tetrahydroxyurs-12-en-28-oate (**5a**) [4], 2α,3β,19α-trihydroxyurs-12-en-28-oic acid **6** [7], dimethyl 2α,3β,19α-trihydroxyurs-12-en-24,28-dioates (**7a**) [8] and 2α,3β,19α-trihydroxyurs-12-en-24,28-dioic acid-24-methyl ester-28-*O*-β-D-glucopyr-



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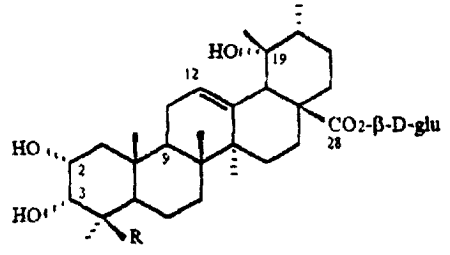

2 R=CH_2OH

3 R=CHO

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Table 1. ^{13}C NMR and DEPT data for compounds **1a**, **2**, **3** and **4**

C	**1a**[a]	DEPT	**2**[b]	DEPT	**3**[b]	DEPT	**4**[a]	DEPT
1	71.2	CH	42.2	CH_2	42.7	CH_2	42.1	CH_2
2	78.9	CH	66.2	CH	72.6	CH	71.6	CH
3	80.7	CH	78.9	CH	78.9	CH	82.3	CH
4	40.6	C	45.1	C	54.0	C	35.4	C
5	53.1	CH	49.5	CH	48.6	CH	49.4	CH
6	18.3	CH_2	19.1	CH_2	18.2	CH_2	18.4	CH_2
7	32.6	CH_2	33.9	CH_2	33.7	CH_2	32.3	CH_2
8	42.9	C	40.8	C	40.5	C	40.0	C
9	47.8	CH	47.8	CH	46.5	CH	46.5	CH
10	37.7	C	38.6	C	38.7	C	38.0	C
11	25.5	CH_2	24.3	CH_2	26.0	CH_2	23.5	CH_2
12	129.8	CH	128.3	CH	128.3	CH	129.3	CH
13	137.3	C	139.2	C	139.2	C	137.7	C
14	41.1	C	42.1	C	42.2	C	41.2	C
15	28.2	CH_2	29.1	CH_2	29.0	CH_2	28.1	CH_2
16	26.0	CH_2	26.0	CH_2	26.6	CH_2	25.3	CH_2
17	47.9	C	48.6	C	48.6	C	47.7	C
18	53.1	CH	54.4	CH	54.4	CH	52.6	CH
19	73.2	C	72.6	C	72.7	C	72.7	C
20	41.1	CH	42.1	CH	42.1	CH	41.1	CH
21	27.3	CH_2	26.7	CH_2	26.0	CH_2	25.9	CH_2
22	37.4	CH_2	37.7	CH_2	37.6	CH_2	37.5	CH_2
23	28.2	CH_3	24.4	CH_3	24.6	CH_3	28.8	CH_3
24	16.1*	CH_3	65.1	CH_2	205.4	C	23.8	CH_3
25	12.0	CH_3	17.3*	CH_3	16.6*	CH_3	15.3*	CH_3
26	16.6*	CH_3	17.2*	CH_3	17.5*	CH_3	16.7*	CH_3
27	24.6	CH_3	24.4	CH_3	20.4	CH_3	24.4	CH_3
28	178.4	C	176.9	C	176.9	C	183.7	C
29	27.4	CH_3	26.9	CH_3	26.9	CH_3	26.5	CH_3
30	17.1*	CH_3	16.6*	CH_3	17.5*	CH_3	16.1*	CH_3
28–CO_2**Me**	51.6	CH_3					isopropylidenyl	
glu-1′			95.8	CH	95.8	CH	28.3	CH_3
2′			74.0	CH	74.0	CH	27.4	CH_3
3′			79.2	CH	79.2	CH	107.0	C
4′			71.2	CH	71.2	CH		
5′			78.9	CH	78.9	CH		
6′			62.3	CH_2	62.3	CH_2		

[a] Run in $CDCl_3$
[b] Run in pyridine-d_5
* interchangeable values in the same column.

anosyl (**8a**) [9] by direct comparison of their spectral data (^1H, ^{13}C NMR and DEPT) with those reported, respectively.

Compound **1a** was obtained as an amorphous powder. Its IR spectrum showed the absorption bands for hydroxyl groups (3435 cm^{-1}), ester carbonyl group (1725 cm^{-1}), and a double bond (1630 cm^{-1}) in the molecule. The EI mass spectrum displayed a molecular ion peak at m/z 518 $[M]^+$, which suggested the molecular formula $C_{31}H_{50}O_6$, and ions at m/z 458 $[M\text{-}60]^+$, 440, 278 and 260. This result was consistent with the ^{13}C NMR and DEPT spectra (Table 1). The characteristic retro–Diels–Alder fragment peaks at m/z 239 (A/B ring) and 278 (D/E ring) indicated a double bond located at C-12, C-13, which suggested a ursane or oleanane skeleton for compound **1a** [10], and trioxygenated substitution on rings A/B, one oxygenated and methyl carbonyl ester substitution on rings D/E. The ^1H NMR spectrum of compound **1a** showed a broad singlet at δ 2.59 (1H, *s*, H-18), which is a characteristic signal for the H-18 of an ursane type with 19-O-substitution, together with six tertiary methyls at δ 0.69, 0.84, 1.02 (2Me), 1.22, 1.27, a methyl doublet at δ 0.94 (3H, *d*, J = 6.6 Hz, Me-30), the ester methyl at δ 3.61 and the olefinic proton at δ 5.37 (1H, *t*, J = 3.8 Hz, H-12). Furthermore, the ^{13}C NMR spectrum of **1a** showed seven methyls and one methyl ester signal, also the olefinic carbon signals at δ 129.8 (CH, C-12) and 137.3 (C, C-13), all of which suggested a 19α-hydroxyurs-12-en type of triterpenoid for compound **1a** [11]. The acetylation of **1a** gave **1b**. In the ^1H NMR spectrum of **1b**, three acetoxyl methyl signals at δ 1.94, 2.00 and 2.15 could be observed [12]. In addition, three acetoxy-bearing methine protons exhibited two doublets at δ 4.11 (J = 8.0 Hz) and δ 5.22 (J = 2.7 Hz) and a double doublet at δ 5.03 (J = 8.0, 2.7 Hz) were assignable to H-3α, H-1β and H-2β, respectively. Three oxygenated methines and one oxygenated quartery carbon were also indicated in the ^{13}C NMR spectrum of **1a** at δ 71.2, 78.9, 80.7 and 73.2. Thus, the structure of **1a** was elucidated as methyl-1α,2α,3β,19α-tetrahydroxyurs-12-en-28-oate, and the naturally occurring compound **1** should be 1α,2α,3β,19α-tetrahydroxyurs-12-en-28-oic acid.

Compound **2**, another amorphous powder, revealed the presence of hydroxyl group (3388 cm^{-1}), ester carbonyl group (1726 cm^{-1}), trisubstituted double bond (1653 cm^{-1}) and glucosidic linkage (1076 cm^{-1}) in its IR spectrum. The FAB mass spectrum showed peaks at *m/z* 689 $[M + Na]^+$, 673 $[M + Li]^+$ and 504 $[M - glu]^-$, which suggested the molecular formula $C_{36}H_{58}O_{11}$ for **2**, and this suggestion was further confirmed by the ^{13}C NMR and DEPT data (Table 1). The ^{13}C NMR spectrum of **2** showed, in addition to 30 signals consistent with a triterpenoid structure, six peaks in the range at δ 62–96 (95.8, 74.0, 79.2, 71.2, 78.9, 62.3) corresponding to the presence of a glucose moiety and the anomeric carbon signal at δ 95.8 (CH) showed an ester linkage with the aglycone [13]. The ^1H NMR spectrum of compound **2** showed a singlet at δ 2.89, the characteristic signal for the H-18 of ursane triterpenoid with 19α-hydroxyl substitution, together with a pair of double bond signals at δ 128.3 (CH, C-12) and 139.2 (C, C-13) in the ^{13}C NMR spectrum, suggested a 19α-hydroxyurs-12-en skeleton for the aglycone of compound **2** [11]. On alkaline hydrolysis compound, **2** gave D-glucose as the sugar component which was identified by direct comparison with an authentic sample.

Comparison of the ^{13}C NMR and DEPT spectral data of **2** with those of 2α,3β,19α,24-tetrahydroxyurs-12-en-28-oic acid-28-*O*-β-D-glucopyranosyl ester, previously identified from the leaves of *Rubus accuminatus* [3], showed that their structures were similar, except that the resonance of the hydroxylated carbons C-2 and C-3 of **2** were shifted upfield at δ 66.2 for C-2 and δ 78.9 for C-3, but the known compound was at δ 68.7 for C-2 and δ 85.8 for C-3. Furthermore, the ^1H NMR spectrum of **2** showed signals at δ 3.83 (*m*, H-2β), δ 3.57 (*br.s*, H-3β), which suggested the α-configuration for the two hydroxy groups on ring A. Compounds reported with a 2α, 3α-diol system [4] had the same chemical shifts for C-2 and C-3 as those for compound **2**. This also confirmed the configuration of 2α, 3α-diol for compound **2**. The ^1H NMR spectrum showed that the glucosyl group was linked with the aglycone in the β-configuration by the anomeric proton at δ 6.30 (*d*, *J* = 8.2 Hz) The ^1H NMR spectrum also revealed the presence of five methyl signals as singlets at α 1.04, 1.16, 1.35, 1.59 and 1.65, a methyl signal as a doublet at δ 1.04 and one olefinic proton signal at δ 5.52 (1H, *br.s*, H-12). Thus, the structure of compound **2** was elucidated as 2α, 3α, 19α, 24-tetrahydroxyurs-12-en-28-oic acid-28-*O*-β-D-glucopyranosyl ester.

Compound **3**, obtained also as an amorphous powder, revealed the presence of a hydroxyl group (3422 cm^{-1}), a carbonyl group (1713 cm^{-1}), a trisubstituted double bond (1647 cm^{-}) and a glucosidic linkage (1068 cm^{-1}) in its IR spectrum. The FAB–mass spectrum showed ions at *m/z* 687 $[M + Na]^+$, 671 $[M + Li]^+$ and 502 $[M - glu]^+$. This result was consistent with the molecular formula $C_{36}H_{56}O_{11}$ previously established on the basis of the ^{13}C NMR and DEPT spectra (Table 1). Its ^{13}C NMR spectrum showed, in addition to 30 signals consistent with triterpenoid, almost the same six peaks in the range δ 62–96 corresponding to the presence of a glucose moiety and ester linkage with the aglycone as those of compound **2**. On alkaline hydrolysis, compound **3** gave D-glucose as the sugar component which was identified by direct comparison with an authentic sample. Furthermore, the ^1H NMR spectrum showed the glucopyranosyl group was linked in the β-configuration for its anomeric proton at δ 6.30 (*d*, *J* = 7.9 Hz). According to the olefinic carbon signals at δ 128.3 (CH, C-12) and 139.2 (C, C-13) in its ^{13}C NMR spectrum, compound **3** had a ursane skeletone [11]. The ^1H NMR spectrum of **3** showed signals of two hydroxy-bearing methines at δ 4.05 (*m*, H-2β) and 3.60 (*br.s*, H-3β), a sharp singlet at δ 2.89 for the 18-H of a 19α-hydroxyurs-12-en system, five methyl singlets, one methyl doublet at δ 1.04 (*J* = 6.4 Hz, Me-30) and an obvious aldehyde proton signal at δ 10.5, consistent with the presence of an aldehyde group, which was confirmed by the ^{13}C NMR signal at δ 205.4 for a formyl group. Comparison of the ^{13}C NMR and DEPT spectral data of the aglycone moiety of compound **3** with those of compound **2**, showed that their structures were very similar, and **3** had the 2α, 3α, 19α-trihydroxyurs-type of structure. In addition, comparison of the spectral data of compound **3** with those of the related compounds [4, 5], showed that the formyl group could be accommodated at the C-24 position in compound **3**. Thus, compound **3** was determined to be 2α,3α,19α-trihydroxyurs-12-en-24-formyl-28-oic acid-28-*O*-β-D-glucopyranosyl ester.

Compound **4** was obtained as colourless crystals. The IR spectrum indicated the presence of a hydroxyl group (3543 cm^{-1}), ester carbonyl group (1728 cm^{-1}), trisubstituted double bond (1675 cm^{-1}) and ether bond (1048 cm^{-1}). The EI mass spectrum displayed a molecular ion peak at *m/z* 528 $[M]^+$ consistent with the molecular formula $C_{33}H_{52}O_5$, which was confirmed by ^{13}C NMR and DEPT data (Table 1). Also the *m/z* 482 $[M–COOH - 1]^+$ and the characteristic retro–Diels–Alder fragment peaks at *m/z* 246 and 264, indicated an ursane or oleanane skeleton for compound **4** [10] with dioxygenated substitution on rings A/B, one oxygenated substitution and one ester methyl substitution on rings D/E. Its ^{13}C NMR and DEPT spectra showed a pair of olefinic carbon signals at δ 129.3 (CH, C-12) and 137.7 (C, C-13), one carbonyl signal at δ 183.7 (C-28), three hydroxylated carbon signals at δ 71.6 (CH, C-2), 82.3 (CH, C-3), 72.7 (C, C-19), and nine methyl signals. Comparison of the ^{13}C NMR data

of **4** with those of the related known compounds 2α,3α,19α-trihydroxyurs-12-en-28-oic acid [4] suggested their structures were similar except for the two additional methyls (δ 28.3, 27.4) and one quaternary carbon (δ 107.0) in **4**. These signals suggested an extra isopropylidene moiety in **4**. Since the C-2 and C-3 signals were shifted downfield about 5.5, and 3.0 ppm, respectively, the position of the isopropylidene was attached to the oxygenated carbon atoms at C-2 and C-3. The ^{1}H NMR spectrum showed a characteristic broad singlet at δ 2.54 (1H, *s*, H-18), together with nine methyls, an olefinic proton at δ 5.34 (*br.s*, H-12), two methine protons at δ 4.22 (*m*, H-2β) and 3.70 (*d*, *J* = 4.3 Hz, H-3β). In conclusion, the structure of compound **4** was identified as 2, 3-*O*-isopropylidenyl-2α,3α,19α-trihydroxyurs-12-en-28-oic acid and it is considered that it could be a artifact.

EXPERIMENTAL

General

Mps: uncorr.; IR (film, MeOH): Nicolet FT-170 SX; Optical rotations: *J*-20C; ^{1}H NMR (400 MHz), ^{13}CNMR (400 MHz) and DEPT spectra: Bruker AM-400 FT–NMR, $CDCl_3$ or pyridine-d_5 as solvent, TMS as int. standard; FABMS and EIMS: VG–ZAB–HS.

Plant material

Aerial parts of *R. Xanthocarpus* were collected in September 1994 at Zhang county, Gansu province, People's Republic of China. It was identified by Prof. Zexiang Peng, Department of Biology, Lanzhou University. A voucher specimen was deposited in the Institute of Organic Chemistry, Lanzhou University.

Extraction and purification

Powdered, dried aerial parts of *R. xanthocarpus* (5 kg) were extracted successively with MeOH at room temp (8 days ×3) and the MeOH extracts were taken to dryness to give 550 g of extract. A suspension of the resulting extract in water (1 l) was washed 3x with petrol (800 ml, 500 ml, 600 ml) and then extracted with EtOAc (3 × 500 ml, each time) and finally extracted with *n*-BuOH saturated with H_2O (3 × 500 ml, each time). The *n*-BuOH extract was taken to dryness to give the crude glycosidic fraction (185 g), which was chromatographed on silica gel (100–180 mesh) using a step-gradient of $CHCl_3$–MeOH–H_2O (30:1:1 to 10:10:1) and finally MeOH to give six frs.(I–VI). Fr. II was divided into two parts fr. II-1 and fr. II-2. Compound **4** was obtained as a pure triterpene from fr. II-1 by repeated CC on silica gel CC with petrol–Me_2CO (10:3) and further purified by prep. TLC (silica GF_{254}) with petrol–Me_2CO (10:3). Fr. II-2 was separated by repeated CC on silica gel with $CHCl_3$–MeOH–H_2O (13:1:0.05) and gave compound **6**. The rest of fr. II-2 was treated with an ethereal solution of CH_2N_2 to yield methyl esters. The methyl esters were separated by CC on silica gel, first with $CHCl_3$–MeOH–H_2O (27:1:0.05), then with petrol–Me_2CO (46:17) and yielded **1a**, **5a** and **7a**. From fr. III, compound **3** was obtained by CC on silica gel with $CHCl_3$–MeOH–H_2O (11:1:0.05). Finally, fr. IV was also treated with an ethereal solution of CH_2N_2 and compounds **2** and **8a** were obtained from the esterified fr. IV by separating on silica gel with $CHCl_3$–MeOH–H_2O (16:1:0.05).

*Methyl 1α,2α,3β,19α-tetrahydroxyurs-12-en-28-oate (**1a**)*

Amorphous powder, $[\alpha]_D^{20}$: −21 ($CHCl_3$, *c* 0.27). IR γ_{max} cm^{-1}: 3435, 1725, 1630. EIMS, *m/z* (rel.int.): 518[M]$^+$(3), 458[M–COOMe-1]$^+$(8), 440(5), 278(2), 260(2), 239(7), 221(5), 219(9), 203(7). ^{1}H NMR: δ 0.94 (*d*, 3H, *J* = 6.6 Hz, Me-30), 0.69, 0.84, 1.02 (2 × Me), 1.22, 1.27 (*s*, 3H each, Me-29, 27, 26, 25, 24, 23), 2.59 (*br.s*, 1H, H-18), 5.37 (*t*, 1H, *J* = 3.8 Hz, H-12), 3.61 (*s*, 3H, OCH_3). ^{13}C NMR and DEPT data see Table 1.

*Triacetate (**1b**) of compound (**1a**)*

^{1}H NMR: δ 4.11 (*d*, 1H, *J* = 8.0 Hz, H-3α), 5.03 (*dd*, 1H, *J* = 8.0, 2.7 Hz, H-2β), 5.22 (*d*, 1H, *J* = 2.7 Hz, H-1β), 1.94, 2.00, 2.15 (*s*, 3H each, 3 × OAc).

*2α,3α,19α,24-tetrahydroxyurs-12-en-28-oic acid-28-O-β-D-glucopyranosyl ester (**2**)*

Amorphous powder, mp: 226–228°C, $[\alpha]_D^{20}$: −27 (MeOH, *c* 0.315). IR γ_{max} cm^{-1}: 3388, 1726, 1653, 1076. FABMS, *m/z* (rel.int.): 689[M + Na]$^+$, 673[M + Li]$^+$, 504[M-glu]$^+$. ^{1}H NMR: δ 6.30 (*d*, 1H, *J* = 8.2 Hz, H-1′), 5.52 (*br.s*, 1H, H-12), 3.83 (*m*, 1H, H-2β), 3.57 (*br.s*, 1H, H-3β), 4.02–4.62 (*m*, 7H, Me-24, H-2′-6′), 2.89 (*s*, 1H, H-18), 1.65, 1.59, 1.35, 1.16, 1.04 (*s*, 3H each, Me-23, 25, 26, 27, 29), 1.04 (*d*, 3H, *J* = 6.4 Hz, Me-30). ^{13}C NMR and DEPT data see Table 1.

*α,3α,19α-Trihydroxyurs-12-en-24-formyl-28-oic acid-28-O-β-D-glucopyranosyl ester (**3**)*

White amorphous powder, mp: 144–146°C, $[\alpha]_D^{20}$: −64 (MeOH, *c* 0.12). IR γ_{max} cm^{-1}: 3422, 1713, 1647, 1068. FABMS, *m/z* (rel. int.): 687[M + Na]$^+$, 671[M + Li]$^+$, 502[M − glu]$^+$. ^{1}H NMR: δ 10.5 (*s*, 1H, H-24), 6.30 (*d*, 1H, *J* = 7.9 Hz, H-1′), 5.50 (*s*, 1H, H-12), 4.05 (*m*, 1H, H-2β), 3.60 (*br.s*, 1H, H-3β), 4.10–4.60 (*m*, 5H, H-2′-6′), 2.89 (*s*, 1H, H-18), 1.57, 1.52, 1.33, 1.18, 0.96 (*s*, 3H each, Me-23, 25, 26, 27, 29), 1.04 (*d*, 3H, *J* = 6.4 Hz, Me-30). ^{13}C NMR and DEPT data see Table 1.

2,3-O-*isopropylidenyl*-2α,3α,19α-*trihydroxyurs*-12-*en*-28-*oic acid* (**4**)

Amorphous crystal. IR γ_{max} cm^{-1}: 3543, 1728, 1675, 1048. EIMS, *m/z* (rel. int.): 528[M]$^+$ (4), 482[M–HCOOH]$^-$(12), 352(3), 264(5), 246(10), 223(8), 149(100). ^{1}H NMR: δ 5.34 (*br.s*, 1H, H-12), 4.22 (*m*, 1H, H-2β), 3.70 (*d*, 1H, *J* = 4.3 Hz, H-3β), 2.54 (*s*, 1H, H-18), 1.49, 1.33, 1.22, 1.07, 0.89, 0.88 (*s*, 3H each, Me-23, 24, 25, 26, 27, 29), 0.96 (*d*, *J* = 6.6 Hz, Me-30), 0.70, 0.89 (*s*, 3H each, 2 × Me of isopropylidenyl). ^{13}C NMR and DEPT data see Table 1.

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