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Phytochemistry 62 (2003) 607–612
PHYTOCHEMISTRY
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Prenylated xanthone glucosides from Ural's lichen *Umbilicaria proboscidea*

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Received 30 July 2002; received in revised form 14 October 2002

Abstract

Two new compounds isolated from an extract of a Central Asian lichen [*Umbilicaria proboscidea* (L.) Schrader = Syn.: *Gyrophora proboscidea* (L.) Ach.] are glucosides with mono- and di-prenylated xanthones as the aglycones and a saccharide moiety from two glucoses linked at C-7. The structures were elucidated on the basis of extensive spectroscopic analysis (1D and 2D NMR, MS, IR and UV) and by hydrolysis.

Keywords: Prenylated xanthones; Xanthone glucosides; Lichen; *Umbilicaria proboscidea*

1. Introduction

Lichens, a symbiotic association of mycobiont and phycobiont organisms, produce a variety of characteristic secondary metabolites (Huneck and Yoshimura, 1996), very frequently colored. Recent studies (Peres et al., 2000; Peres and Nagem, 1997) describe many hundreds of xanthones identified in addition to higher plants and also a few in lichens (Tanahashi et al., 1999). According to the literature data, only a few phytochemical research studies were carried out on lichens.

As a constitution of our search for compounds from lichens, we examined constituents of the lichen *Umbilicaria proboscidea*, collected in Ural Mountains, Muslimovo Village, 50 km west from Chelyabinsk (Russia). Many lichen species have been studied and xanthones and other colored compounds have been identified as their constituents (Peres et al., 2000; Peres and Nagem, 1997). In contrast, only the depsides and tridepsides from the genus of *Umbilicaria* (family Umbilicariaceae) were described in the literature (Serina et al., 1996; Narui et al., 1998; Huneck et al., 1993). In the previous papers (Řezanka and Guschina, 2000, 2001a,b,c), we reported on the isolation and identification of many natural compounds from lichens of the Tien Shan Mountains. In this paper, we describe the isolation and identification of two new xanthone glycosides, umbilicaxanthosides A (**1**) and B (**2**), from the lichen *U. proboscidea* collected in Russia. These compounds were described for the first time in nature.

2. Results and discussion

The lichen was dried and extracted successively with $CHCl_3$ and MeOH. The MeOH extract was subjected to gel filtration on Sephadex LH-20. Subsequent chromatography by RP-HPLC led to the isolation of new xanthone glycosides, umbilicaxanthosides A (**1**) and B (**2**).

Umbilicaxanthoside A (**1**) crystallized as pale yellow needles, with mp 114 °C. The HRFABMS showed a pseudomolecular ion at m/z 505.1713 $[M+H]^+$, and established a molecular formula of $C_{25}H_{28}O_{11}$. The fragment at m/z 341 $[M-H-162]^-$ was also observed in negative FABMS, suggesting that there was one hexose moiety in the molecule. The IR spectrum indicated the presence of hydroxyl groups and a conjugated carbonyl group from bands at 3320 and 1643 cm^{-1}, respectively.

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0031-9422/03/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0031-9422(02)00539-3

The UV spectrum exhibited characteristic absorption bands (Chaudhuri and Ghosal, 1971) of the xanthone at λ_{max} 245, 270, 310 and 345 nm. The ^{13}C NMR spectrum of **1** showed signals for 25 carbons in the molecule, with six monosaccharide carbons, including an anomeric carbon at δ 99.8 and 19 carbons corresponding to an aglycone moiety, with a carbonyl carbon at δ 179.8 (C-9). In the ^1H NMR spectrum of **1**, the signals of five oxymethine protons in diaxial conformations ($J = 7.0$–9.0 Hz) and one oxymethylene group indicated the presence of a glucopyranosyl group. By acid hydrolysis with HCl but also enzymatic hydrolysis with β-D-glucosidase (EC 3.2.1.21), **1** was liberated to give an aglycone (**1a**) and β-D-glucose. The β configuration of the anomeric center was also determined by the ^1H NMR ($J = 7.3$ Hz) and ^{13}C NMR (C-1″ at δ 99.8) data (Breitmaier and Voelter, 1987).

Compound **1a** gave a pseudomolecular ion at m/z 343.1184 in its HRFABMS $[M+H]^+$, corresponding to the elemental formula $C_{19}H_{18}O_6$. The UV spectrum of **1a** was also typical of the xanthone nucleus (Somanathan and Sultanbawa, 1974). The IR spectrum showed an absorption band at 3320 cm^{-1} for hydroxyl groups and at 1645 cm^{-1} for a conjugated carbonyl functionality that also appeared at δ_C 179.8 (C-9) in the ^{13}C NMR spectrum of **1a**. This carbonyl group formed a hydrogen bond with a hydroxyl group, as evidenced by a proton signal at δ_H 13.25 (OH-1). Three aromatic proton signals were observed at δ_H 6.51 (H-3), 6.39 (H-6) and 6.50 (H-8) and six oxygenated aromatic carbon signals appeared at δ_C 150.9 (C-1), 120.1 (C-3), 140.9 (C-4a), 146.4 (C-5), 136.5 (C-5a) and 156.9 (C-7). The ^1H NMR spectrum of **1a** showed the presence of characteristic *meta*-coupled aromatic protons ($\delta_{H\text{-}6}$ 6.15, *d*, $J = 2.1$ Hz; $\delta_{H\text{-}8}$ 6.50, *d*, $J = 2.1$ Hz).

The signal of one methoxyl group was found in the NMR spectrum of **1a**; the ^1H NMR signals at δ_H 3.75 integrated as three protons and showed a cross-peak with the ^{13}C NMR signals at δ_C 56.4. The methoxyl group was positioned at C-4 by two-bond HMBC (Fig. 1) connectivities of H-3/C-4 and OCH_3-4/C-4. Signals at δ_H 3.19/δ_C 22.0 (C-1′), 5.92/123.5 (C-2′), 1.64/25.9 (C-4′), 1.57/17.9 (C-5′), and δ_C 131.3 (C-3′) were due to a prenyl group by comparison of the NMR data with literature values (Sia et al., 1995). The prenyl group was assigned to C-2 based on the HMBC correlations of H-1′/C-2 (two-bond), H-1′/C-l (three-bond), and H-1′/C-3 (three-bond). Thus, the structure of the new xanthone (**1a**) was assigned as 1,5,7-trihydroxy-4-methoxy-2-(3-methyl-2-butenyl)-9*H*-xanthen-9-one (umbilicaxanthone A).

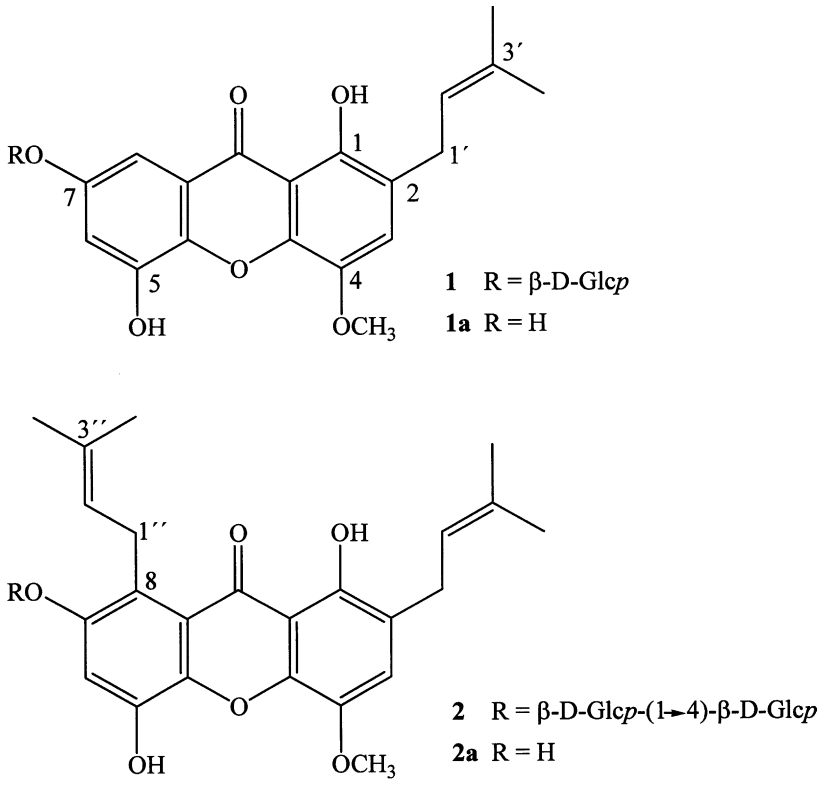
In the ^1H NMR spectrum of **1**, the unusual 7-*O*-glycosylation was indicated by downfield shifts (Markham et al., 1978) of H-6 (+0.24 ppm) and H-8 (+0.23 ppm) with respect to aglycone (**1a**) as the comparative compound. Similarly, in the ^{13}C NMR spectra of **1** (Table 1) 7-*O*-glycosylation was confirmed by the diagnostic downfield shift of C-7 (+3.9 ppm) and by upfield shift of the related C-6 (−2.7 ppm) and C-8 (−1.8 ppm) carbons with respect to aglycone **1a**, suggested the location of a glucose moiety at the 7-hydroxyl group.

Thus, the structure of umbilicaxanthoside A (**1**) was established as 7-[(β-D-glucopyranosyl)oxy]-1,5-dihydroxy-4-methoxy-2-(3-methyl-2-butenyl)-9*H*-xanthen-9-one.

Umbilicaxanthoside B (**2**) crystallized as pale yellow needles, mp 133 °C. The HRFABMS established the molecular formula **2** as $C_{36}H_{46}O_{16}$ i.e. $[M+H]^+$ at m/z 735.2868. Negative FABMS gave three prominent ions at m/z 733 $[M-H]^-$, m/z 571 $[M-H-162]^-$ and m/z 409 $[M-H-2\times162]^-$ corresponding to the loss of one and/or two hexoses, respectively. Acid hydrolysis of **2** with 2 N hydrochloric acid yielded glucose and aglycone. Enzymatic hydrolysis of **2** by β-D-glucosidase (EC 3.2.1.21) gave again β-D-glucose. These results reveal that **2a** contains only β-D-glucose.

Compound **2a** was deduced to have an elemental formula of $C_{24}H_{26}O_6$ by HRFABMS, which showed a pseudomolecular ion peak $[M+1]^+$ at m/z 411.1810 (calc. 411.1807). The IR spectrum showed an absorption band at 3350 cm^{-1} for hydroxyl groups and 1640 cm^{-1} for conjugated carbonyl functionality. The UV, ^1H and ^{13}C NMR spectra indicated the presence of a xanthone skeleton as in **1a**. The ^1H and ^{13}C NMR spectra of **2a** were similar to those of compound **1a** except for the presence of signals for a further prenyl group at δ_H 4.19/δ_C 26.1 (C-1″), 5.37/124.8 (C-2″), 1.67/25.9 (C-4″), 1.84/18.0 (C-5″), and δ_C 132.0 (C-3″) instead of signal for the hydrogen of **1a**. One prenyl group was assigned to C-2 by a two-bond correlation of H-1′/C-2 and three-bond connectivities of H-1′/C-1 and H-1′/C-3. The second prenyl group was positioned at C-8, as evidenced by correlations of H-1″/C-8 (two-bond), H-1″/C-7 (three-bond), and H-1″/C-8a (three-bond). A proton signal for H-1″ appeared at δ_H 4.19, which is a more deshielded value than usually found for this functionality, due to the carbonyl group effect described in literature (Somanathan and Sultanbawa, 1972), and thus provided further evidence for the position of the prenyl group at C-8. Therefore, the new prenylated xanthone **2a** was assigned as 1,5,7-trihydroxy-4-methoxy-2,8-diprenyl-9*H*-xanthen-9-one (umbilicaxanthone B).

The ^1H and ^{13}C NMR data of **2** (Table 2) were similar to those of umbilicaxanthoside A (**1**), but **2** had an additional glucose moiety. The ^1H NMR spectrum of **2** showed the presence of two aromatic hydrogens and the monosaccharide moieties including two anomeric protons at δ 5.05 ($J = 8.1$ Hz, H-1‴) and δ 5.15 ($J = 8.0$ Hz, H-1⁗). The ^{13}C NMR spectrum of **2** showed 36 signals, of which 12 were assigned to the monosaccharide protons and 24 to a tetraoxygenated xanthone moiety. The monosaccharide proton resonances were assigned based on the ^1H–^1H COSY spectrum, and the ^{13}C NMR data



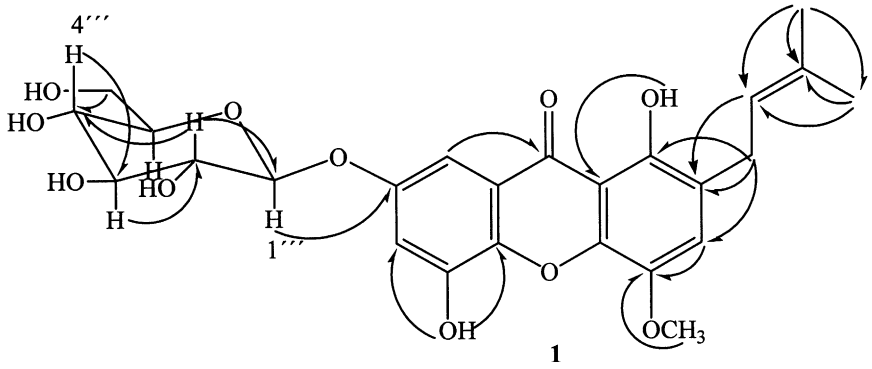


Fig. 1. Some important HMBC correlations of compound **1**.

were assigned from the HMBC spectrum. The NMR data of **2** (Table 2) indicated that it contains the two glucoses.

In **2** a glycosidation shift (Tori et al., 1977) at C-4‴ (ca. +8.5 ppm) and the chemical shifts of H-1‴ (δ 5.05) and C-1‴ (δ 99.8) of glucose indicated that this monosaccharide was glycosylated at C-4‴ and linked with the aglycone. The one signal due to the anomeric proton of glucose (δ 5.15, *d*, J=8.0 Hz), correlating to the C-1⁗ resonance at δ 104.1 by the HMBC spectrum indicated that the glucose unit was linked with a secondary alcoholic carbon (C-4‴ of the first glucose). By HOHAHA, this proton showed connectivities with a signal δ 3.58 (1H, *t*, J=8.9, H-4‴ by COSY), which was correlated by HMBC to a carbon resonance at δ 78.2 (C-4‴) showing glycosylation at position 4‴. Glucose was determined to be terminal by the absence of any glycosylation shift. These deductions were confirmed by the HMBC spectrum, which showed some diagnostic long-range correlations between H-1‴ of the first glucose (δ 5.05) and C-7 (δ 153.2) of the aglycone (Seo et al., 1978; Tori et al., 1977), between H-1⁗ (δ 5.15) of the second glucose unit and C-4‴ (δ 78.2) of the first glucose. Thus, the structure of xanthoside was established as 7-[(β-D-

Table 1
^{1}H and ^{13}C NMR spectral data for umbilicaxanthoside A (**1**) and umbilicaxanthone (**1a**)

Position	**1**		**1a**	
	^{13}C	^{1}H (*J*)	^{13}C	^{1}H (*J*)
1	150.9	–	150.9	–
2	118.2	–	118.2	–
3	120.1	6.51 (1H, *s*)	120.1	6.51 (1H, *s*)
4	142.6	–	142.6	–
4a	140.9	–	140.9	–
5a	136.5	–	136.5	–
5	146.4	–	146.4	–
6	104.8	6.39 (1H, *d*, *J* = 2.1 Hz)	102.1	6.15 (1H, *d*, *J* = 2.1 Hz)
7	153.0	–	156.9	–
8	108.1	6.73 (1H, *d*, *J* = 2.1 Hz)	106.3	–
8a	128.9	–	128.9	–
9	179.8	–	179.8	–
9a	116.1	–	116.1	–
1-OH	–	13.25 *s*	–	13.25 *s*
3-OCH_3	56.4	3.75 (3H, *s*)	56.4	3.75 (3H, *s*)
1′	22.0	3.19 (2H, *d*, *J* = 6.6 Hz)	22.0	3.19 (2H, *d*, *J* = 6.6) Hz
2′	123.5	5.92 (1H, *td*, *J* = 6.6, 1.3 Hz)	123.5	5.92 (1H, *td*, *J* = 6.6, 1.3 Hz)
3′	131.3	–	131.3	–
4′	25.9	1.64 (3H, *s*)	25.9	1.64 (3H, *s*)
5′	17.9	1.57 (3H, *s*)	17.9	1.57 (3H, *s*)
1″	99.8	4.80 (1H, *d*, *J* = 7.3 Hz)	–	–
2″	74.7	3.52 (1H, *dd*, *J* = 8.9, 7.3 Hz)	–	–
3″	77.2	3.58 (1H, *t*, *J* = 8.9 Hz)	–	–
4″	71.4	3.41 (1H, *t*, *J* = 8.9 Hz)	–	–
5″	78.6	3.45 (1H, *m*)	–	–
6″	62.6	3.72 (1H, *dd*, *J* = 12.1, 5.2 Hz) 3.93 (1H, *dd*, *J* = 11.8, 2.3 Hz)	–	–

glucopyranosyl-(1→4)-β-D-glucopyranosyl)oxy]-1,5-dihydroxy-4-methoxy-2,8-di-(3-methyl-2-butenyl)-9*H*-xanthen-9-one (**2**) (umbilicaxanthoside B).

Many mono- and di-prenyl xanthone derivatives were isolated from plants (Peres et al., 2000; Peres and Nagem, 1997) but the occurrence of a prenyl group at C-8 of a xanthone molecule is unusual and this type of compound from lichens has not been yet reported. The xanthone glycosides have frequently been described in higher plants, especially recently (Kobayashi et al., 2000; Yang et al., 2002) but only a few reports which describe the presence of glycosides from lichens were published (Huneck and Yoshimura, 1996; Řezanka and Guschina, 2001a,b,c). To our best knowledge, this is the first report describing prenylated glycosides of xanthones in lichens.

3. Experimental

3.1. General experimental procedures

UV–vis spectra were measured in MeOH within the range of 220 to 550 nm in a Cary 118 (Varian) apparatus. A Perkin-Elmer model 1310 (Perkin-Elmer, Norwalk, CT, USA) IR spectrophotometer was used for scanning IR spectroscopy as neat films. Optical rotations were described in a Perkin-Elmer polarimeter 343. NMR spectra were recorded on a Brüker AMX 500 spectrometer (Bruker Analytik, Karlsruhe, Germany) at 500.1 MHz (^{1}H), 125.7 MHz (^{13}C). High- and also low-resolution MS were recorded using a VG 7070E-HF spectrometer (70 eV). HRFABMS (positive and/or negative ion mode) were obtained with a PEG-400 matrix. Gas chromatography analysis was in a Hewlett Packard HP 5980 gas chromatograph (Hewlett Packard, Czech Republic).

3.2. Plant material

The specimen of lichen *Umbilicaria proboscidea*, was collected in August 2001 in Ural Mountains, Muslimovo Village, 50 km from Chelyabinsk (Russia). The voucher specimen was identified by the co-author and designated as UP 12082001/11A. It is deposited in the collection of the third author (V.M. Dembitsky).

3.3. Extraction and isolation

The aqueous-MeOH layer (Blight and Dyer, 1959) of lipid extracts from 100 g of air-dried lichens (see Řezanka and Guschina, 2000) was separated on a

Table 2
^{1}H and ^{13}C NMR spectral data for umbilicaxanthoside B (**2**) and umbilicaxanthone (**2a**)

Position	**2**		**2a**	
	^{13}C	^{1}H (*J*)	^{13}C	^{1}H (*J*)
1	151.0	–	151.0	–
2	117.8	–	117.8	–
3	119.4	6.47 (1H, *s*)	119.4	6.49 (1H, *s*)
4	143.2	–	143.2	–
4a	141.3	–	141.3	–
5a	135.7	–	135.7	–
5	147.1	–	146.2	–
6	103.7	6.23 (1H, *s*)	102.4	6.27 (1H, *s*)
7	153.2	–	157.2	–
8	118.4	–	117.6	–
8a	129.6	–	129.6	–
9	183.1	–	183.1	–
9a	114.6	–	114.6	–
1-OH	–	13.30 *s*	–	13.30 *s*
3-OCH_3	56.3	3.75 (3H, *s*)	56.4	3.75 (3H, *s*)
1′	25.4	3.38 (2H, *d*, *J* = 7.2 Hz)	25.4	3.38 (2H, *d*, *J* = 7.2 Hz)
2′	123.8	5.39 (1H, *dd*, *J* = 7.2, 1.2 Hz)	123.8	5.39 (1H, *dd*, *J* = 7.2, 1.2 Hz)
3′	130.9	–	130.9	–
4′	26.2	1.65 (3H, *s*)	26.2	1.65 (3H, *s*)
5′	18.4	1.79 (3H, *s*)	18.4	1.79 (3H, *s*)
1″	26.1	4.19 (2H, *d*, *J* = 6.8 Hz)	26.1	4.19 (2H, *d*, *J* = 6.8 Hz)
2″	124.8	5.37 (1H, *td*, *J* = 6.8, 1.5 Hz)	124.8	5.37 (1H, *td*, *J* = 6.8, 1.5 Hz)
3″	132.0		132.0	
4″	25.9	1.67 (3H, *s*)	25.9	1.67 (3H, *s*)
5″	18.0	1.84 (3H, *s*)	18.0	1.84 (3H, *s*)
1‴	99.8	5.05 (1H, *d*, *J* = 8.1 Hz)	–	–
2‴	74.2	3.52 (1H, *dd*, *J* = 8.9, 8.1 Hz)	–	–
3‴	76.9	3.58 (1H, *t*, *J* = 8.9 Hz)	–	–
4‴	78.2	3.12 (1H, *dd*, *J* = 9.3, 8.9 Hz)	–	–
5‴	78.7	3.45 (1H, *m*)	–	–
6‴	62.6	3.72 (1H, *dd*, *J* = 12.1, 5.2 Hz) 3.93 (1H, *dd*, *J* = 12.1, 2.3 Hz)	–	–
1⁗	104.1	5.15 (1H, *d*, *J* = 8.0 Hz)	–	–
2⁗	73.8	3.52 (1H, *dd*, *J* = 9.0, 8.0 Hz)	–	–
3⁗	76.5	3.58 (1H, *t*, *J* = 9.0 Hz)	–	–
4⁗	69.7	3.41 (1H, *t*, *J* = 9.0 Hz)	–	–
5⁗	76.9	3.45 (1H, *m*)	–	–
6⁗	62.6	3.72 (1H, *dd*, *J* = 12.1, 5.2 Hz) 3.93 (1H, *dd*, *J* = 12.1, 2.2 Hz)	–	–

Sephadex LH-20 column eluted with MeOH–H_2O (9:1) yielding a yellow powder. This powder was further fractionated by RP-HPLC on a C18-Bondapak column (30 cm×7.8 mm, flow rate 2.0 ml/min) eluted with MeCN–H_2O (1:2) to yield compounds **1** (5.4 mg) and **2** (12.3 mg).

3.4. Hydrolysis of glycosides

Glycosides (~0.5 mg) were refluxed in 2 N HCl (0.5 ml) for 2 h. The aglycone was extracted three times with ethyl acetate (10 ml). After separation of the organic layer, the aqueous phase was neutralized with $NaHCO_3$ and lyophilized. The lyophilizate was silylated by TMCS–HMDS and identified by GC. The identification of the monosaccharide was carried out by comparison with authentic sugar marker (Glc) under the same conditions.

A solution of glycoside (4.0 mg) in acetate buffer (pH 4.4, 10 ml) was treated with β-glucosidase (20 mg) for 48 h at 37 °C. The reaction solution was evaporated to dryness, and the residue was chromatographed on a column of silica gel (10 g), using CH_2Cl_2–MeOH–H_2O (90:10:1) to provide xanthone for ^{1}H NMR analysis. The retention times of glucose were 20.47 and 21.66 min for α and β-TMS Glc, respectively.

Umbilicaxanthoside A (**1**), (5.4 mg), pale yellow needles, mp 114 °C; $[\alpha]_D^{23}$ −35°; UV λ_{max} (MeOH, nm) 245 (log ε 4.50), 270 (log ε 4.05), 310 (log ε 4.15) and 345 (log ε 3.90); IR (KBr) 3320 (OH), 2945, 2905, 1643 (C=C–C=O) cm^{-1}; HRFABMS *m*/*z* 505.1713 $[M+H]^+$, calculated for $[C_{25}H_{23}O_{11}+H]^+$ 505.1709;

negative FABMS m/z 503 $[M-H]^-$ and m/z 341 $[MH-162]^-$; for ^1H and ^{13}C NMR spectra, see Table 1.

Umbilicaxanthone A (**1a**), yield after hydrolysis of **1** was 62% (2.52 mg), yellow crystals, mp 165 °C; UV λ_{max} (MeOH, nm) 242 (log ε 4.12), 273 (log ε 4.01), 318 (log ε 4.12) and 351 (log ε 4.00); IR (KBr) 3320 (OH), 1645 (C=C–C=O) cm^{-1}; HRFABMS m/z 343.1184 $[M+H]^+$, calculated for $[C_{19}H_{18}O_6+H]^+$ m/z 343.1181; for ^1H and ^{13}C NMR spectra, see Table 1.

Umbilicaxanthoside B (**2**), (12.3 mg), pale yellow needles, mp 133 °C; $[\alpha]_D^{23}$ −47°; UV λ_{max} (MeOH, nm) 244 (log ε 4.08), 271 (log ε 3.96), 319 (log ε 4.01) and 355 (log ε 4.06); IR (KBr) 3350 (OH), 2950, 2900, 1640 (C=C–C=O) cm^{-1}; HRFABMS m/z 735.2868 $[M+H]^+$, calculated for $[C_{36}H_{46}O_{16}+H]^+$, m/z 735.2863; negative FABMS m/z 733 $(M-H)^-$, m/z 571 $(M-H-162)^-$ and m/z 409 $(M-H-2\times162)^-$; for ^1H and ^{13}C NMR spectra, see Table 2.

Umbilicaxanthone B (**2a**), yield after hydrolysis of **2** was 73% (2.92 mg), yellow crystals, mp 170 °C; UV λ_{max} (MeOH, nm) 243 (log ε 3.97), 276 (log ε 3.90), 318 (log ε 4.11) and 354 (log ε 4.09); IR (KBr) 3350 (OH), 1640 (C=C–C=O) cm^{-1}; HRFABMS m/z 411.1810 $[M+H]^+$, calculated for $[C_{24}H_{26}O_6+H]^+$ m/z 411.1807; for ^1H and ^{13}C NMR spectra, see Table 2.

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