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Three acylated flavone glycosides from *Sideritis ozturkii* Aytac & Aksoy

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Abstract

From the aerial parts of *Sideritis ozturkii*, three new flavonoids, chrysoeriol 7-*O*-[2‴-*O*-caffeoyl-6‴-*O*-acetyl-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside], chrysoeriol 7-*O*-[2‴-*O*-caffeoyl-β-D-glucopyranosyl-(1→ 2)-β-D-glucopyranoside] and chrysoeriol 7-*O*-[2‴-*O*-*p*-coumaroyl-6‴-β-*O*-acetyl-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside] named as ozturkosides A, B and C, respectively, were isolated, along with three known phenylethanoid glycosides, verbascoside, leucoseptoside A, martynoside and five known diterpenoids, 7-epicandicandiol, linearol, sidol, sideroxol, epoxyisolinearol. The structures were elucidated mainly by spectroscopic methods.

Keywords: *Sideritis ozturkii*; Lamiaceae; Flavonoids; Acylated flavone glycosides; Phenylethanoids; Diterpenoids

1. Introduction

The genus *Sideritis* L. (Lamiaceae) is represented by more than 150 species which are distributed especially in Mediterranean region (Obon de Castro and Rivera-Nunez, 1994). In Turkey 46 species are growing (Aytac and Aksoy, 2000) and some of which have been used in traditional medicine and as herbal tea (Baytop, 1999). The genus is known to be rich in essential oils (Ezer et al., 1996; Baser, 2002), diterpenes (Topcu et al., 2002), flavonoids and phenylethanoid glycosides (Ezer et al., 1992; Ezer and Akcos, 1995; Akcos et al., 1999). As a part of our continuing phytochemical studies on *Sideritis* species, here in we report the isolation and structure elucidation of three new flavonoids, named ozturkosides A, B, C (**1**–**3**), from the acetone extract of the aerial parts of *S. ozturkii* Aytac & Aksoy together with known phenylethanoid glycosides (verbascoside, leucoseptoside A, martynoside) and diterpenoids (7-epicandicandiol, linearol, sidol, sideroxol, epoxyisolinearol). *S. ozturkii* is an endemic species and a new record for the flora of Turkey.

2. Results and discussion

VLC, repeated column chromatography (polyamide and silica gel) and MPLC of acetone extract of the aerial parts of *S. ozturkii* yielded compounds **1**–**11** (Fig. 1). Compound **1** was isolated as an amorphous yellow powder. The ^{1}H and ^{13}C NMR spectra of **1** demonstrated the presence of aromatic systems, sugar moieties and olefinic protons. The UV spectrum exhibited maxima at 250 (sh), 270, 337 nm and spectroscopic data with diagnostic reagents were indicative of a flavone skeleton (Mabry et al., 1970). The IR spectrum indicated absorption bands for hydroxyl (3353 cm^{-1}), ester carbonyl (1715 cm^{-1}), γ-pyrone carbonyl (1657 cm^{-1}) and aromatic rings (1602, 1516 cm^{-1}). The negative ion mode ESI mass spectrum showed a signal at *m/z* 827 $[M-H]^-$, compatible with the molecular formula $C_{39}H_{40}O_{20}$. In the ^{1}H NMR spectrum of **1** (Table 1) the presence of

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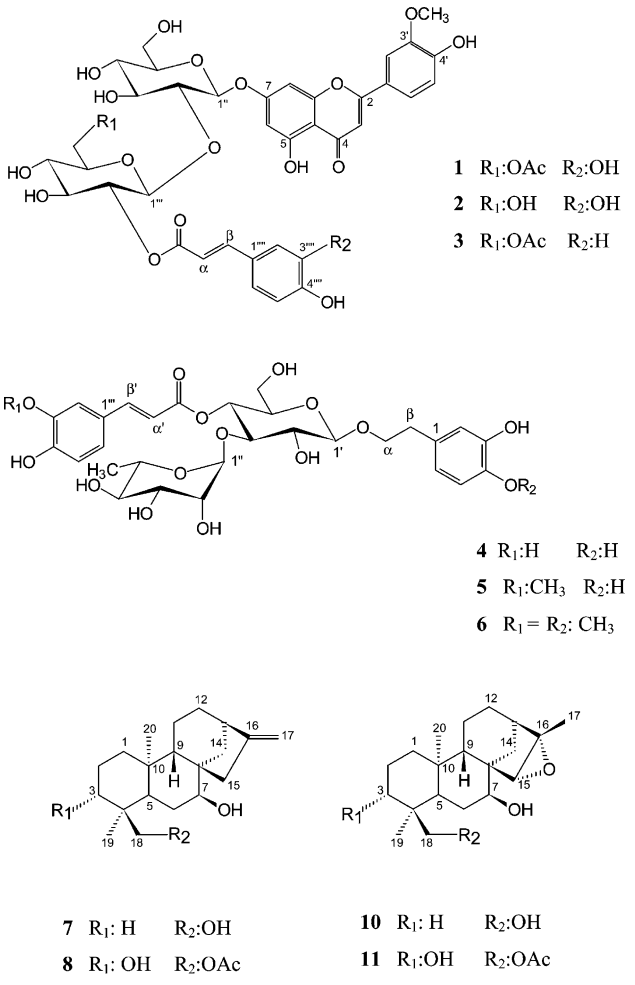

Fig. 1. Compounds isolated from *Sideritis ozturkii*.

disubtituted ring B was confirmed by an ABX pattern signals at δ_H 7.58 (d, $J = 2.2$ Hz, H-2′), 7.56 (dd, $J = 2.2$, 8.2 Hz, H-6′) and 6.94 (H-5). Furthermore, in the aromatic region, two *meta*-coupled doublets at δ_H 6.42 (d, $J = 2.0$ Hz, H-6) and 6.76 (d, $J = 2.0$ Hz, H-8) were characteristic of the 5,7-disubstituted A ring of flavonoid. Singlet signal at δ_H 6.93 was attributed to H-3. In the ^{1}H NMR spectrum of **1**, signals at δ_H 3.90 (s, 3H) and 2.00 (s, 3H) also revealed the presence of a methoxyl group and acetoxymethyl function, respectively. Unambiguous assignment for the ^{1}H and ^{13}C NMR signals in **1** were made by combination of the DQF-COSY, HSQC, HMBC and ROESY experiments. Therefore, according to established NMR data of **1**, the structure of the aglycone moiety was shown to be chrysoeriol (Calis et al., 2002). Two anomeric proton resonances of the disaccharide at δ_H 5.20 (d, $J = 7.8$) and 4.91 (d, $J = 8.1$) were used in conjunction with DQF-COSY and HSQC data to assign the ^{1}H and ^{13}C NMR resonances of sugars and identified both of them as β-glucopyranose (Klimek, 1988). The downfield of C-2″ of terminal glucose to δ_C 80.1 characterized the interglycosidic linkage between these sugars $(1 \rightarrow 2)$. The ^{13}C NMR and DEPT-135 spectra of **1** showed, 39 carbon resonances (14C, 21CH, $2CH_2$ and $2CH_3$), 16 of which could be assigned to chrysoeriol, 12 for two hexosyl units and 2 for an acetyl function. The remaining 9 resonances were consistent with the presence of caffeic acid (Klimek, 1988). The ^{1}H NMR spectrum of **1** showed three aromatic protons as an ABX system [δ_H 7.02 (d, $J = 2.0$ Hz, H-2‴), 6.74 (d, $J = 8.1$ Hz, H-5‴), 6.95 (dd, $J = 2.0$, 8.1 Hz, H-6‴)] and two olefinic protons at δ_H 6.24 d and 7.44 d ($J_{AX} = 15.9$ Hz, indicating *trans*-geometry) which appeared as an AX system were characteristic of *trans*-caffeoyl. The significant deshielding of H-2‴ of terminal glucose (δ_H 4.61) and HMBC cross-peak between this proton and the carbonyl carbon of caffeic acid at δ_C 165.9 confirmed that the caffeoyl residue was connected at H-2‴ via ester linkage. Additionally, the long-range correlations between the anomeric proton of the terminal glucose (δ_H 4.91, H-1‴) and C-2″ of inner glucose (δ_C 80.1), and the anomeric proton of the inner glucose (δ_H 5.20, H-1″) and C-7 of chrysoeriol (δ_C 162.7) demonstrated the $(1 \rightarrow 2)$ interglycosidic linkage between two glucosyl units and the site of glycosidation at C-7 of chrysoeriol moiety. HMBC spectrum also indicated the long-range couplings between carbonyl carbon of acetoxyl function (δ_C 170.4) and H-6‴ representing the hydroxyl group at C-6‴ of terminal glucose was involved in the ester linkage. On the other hand, the methoxyl singlet at (δ_H 3.90) was correlated with C-3′ carbon resonance (δ_C 148.1) showing the attachment of the methoxyl group at C-3′ of ring B. In the ROESY spectrum, ROE correlations between the anomeric proton of the inner glucose and H-6 and H-8 protons of the aglycone, the anomeric proton of the terminal glucose and H-2″ confirmed the suggested structure. Based on these data, the structure of compound **1** was established as chrysoeriol 7-*O*-[2‴-*O*-caffeoyl-6‴-*O*-acetyl-β-D-glucopyranosyl-$(1 \rightarrow 2)$-β-D-glucopyranoside], for which the trivial name ozturkoside A is proposed.

Compounds **2** and **3** were obtained as amorphous yellow powders. The molecular formulas of them were determined to be $C_{37}H_{38}O_{19}$ and $C_{39}H_{40}O_{19}$, respectively, by negative ion mode ESI mass spectra (m/z 785 $[M-H]^-$and 811 $[M-H]^-$, respectively), ^{13}C NMR and DEPT. The UV absorptions recorded with shifting reagents (λ_{max} 250 (sh), 270, 336 and 250 (sh), 271, 330 nm, respectively) and the IR spectrum were very similar to those of compound **1**. When comparing their NMR data (Table 1), a striking resemblance was noticed between **1** and **2**. The only difference was the absence of the acetyl signals in the spectra of **2**. This assumption was proved by the chemical shift value of C-6‴ (δ_C 60.5) resonance of the terminal glucose moiety, exhibiting no unusual shift due to an acylation. The NMR data of **3** (Table 1) showed that it possessed identical aglycone and sugar structures to

Table 1
^{13}C and ^{1}H NMR spectroscopic data[a] for **1**–**3** (DMSO-d_6)

C/H	δ_C ppm			δ_H ppm (J, Hz)		
Atom	**1**	**2**	**3**	**1**	**2**	**3**
Aglycone						
2	164.2	164.1	164.2			
3	103.5	103.4	103.4	6.93 s	6.93 s	6.94 s
4	182.1	182.0	182.0			
5	161.2	161.1	161.1			
6	99.3	99.6	99.3	6.42 d (2.0)	6.46 d (2.0)	6.42 d (2.0)
7	162.7	162.7	162.6			
8	94.8	95.1	94.8	6.76 d (2.0)	6.85 d (2.0)	6.74 d (2.0)
9	156.9	156.9	156.9			
10	105.3	105.3	105.3			
1′	121.2	121.3	121.1			
2′	110.3	110.3	110.2	7.58 d (2.2)	7.56 d (2.0)	7.56[b]
3′	148.1	148.1	148.1			
4′	151.0	151.1	151.2			
5′	115.8	115.8	115.7	6.94[b]	6.94 d (8.0)	6.94 d (7.7)
6′	120.5	120.5	120.5	7.56 dd (2.2, 8.2)	7.57 dd (2.0, 8.0)	7.57[b]
OCH_3	56.0	56.3	56.9	3.90 s	3.89 s	3.89 s
Glucose						
1″	97.5	97.7	97.3	5.20 d (7.8)	5.20 d (8.1)	5.20 d (7.8)
2″	80.1	79.6	80.0	3.52 dd (7.8, 8.9)	3.56 dd (8.1, 9.5)	3.50 dd (7.8, 8.8)
3″	76.1	75.9	75.9	3.38[b]	3.40[b]	3.37[b]
4″	69.9	69.9	69.9	3.26[b]	3.22[b]	3.25[b]
5″	76.7	76.7	76.7	3.46[b]	3.44[b]	3.44[b]
6″	60.4	60.6	60.4	3.45 dd (4.6, 10.5)	3.49 dd (4.8, 11.5)	3.44[b]
				3.68[b]	3.58[b]	3.66 br d (12.0)
Glucose						
1‴	100.7	100.1	100.4	4.91 d (8.1)	4.92 d (8.1)	4.91 d (8.1)
2‴	73.7	73.9	73.6	4.61 dd (8.1, 9.4)	4.59 dd (8.1, 9.5)	4.61 dd (8.1, 9.3)
3‴	74.1	74.5	74.1	3.43[b]	3.41[b]	3.43[b]
4‴	69.8	69.7	69.7	3.20[b]	3.17[b]	3.18[b]
5‴	73.5	76.8	73.5	3.44[b]	3.19[b]	3.45[b]
6‴	63.1	60.5	63.1	4.13[b]	3.65 dd (2.0, 12.2)	4.13 dd (2.0, 12.2)
				4.19 dd (1.9, 12.2)	3.43[b]	4.20 br d (12.2)
Caffeic (Coumaric) acid						
1⁗	125.7	125.6	125.2			
2⁗	114.8	114.7	130.1	7.02 d (2.0)	6.99 d (1.8)	7.49 d (8.5)
3⁗	148.2	148.3	115.7			6.79 d (8.5)
4⁗	145.6	145.6	159.7			
5⁗	115.7	115.7	115.7	6.74 d (8.1)	6.71 d (8.1)	6.79 d (8.5)
6⁗	121.4	121.1	130.1	6.95 dd (2.0, 8.1)	6.92 dd (1.8, 8.1)	7.49 d (8.5)
α	114.7	114.6	114.8	6.24 d (15.9)	6.20 d (15.9)	6.32 d (15.9)
β	144.6	144.5	144.2	7.44 d (15.9)	7.40 d (15.9)	7.50 d (15.9)
C=O	165.9	165.8	165.9			
$COCH_3$	20.7		20.6	2.00 s		2.01 s
$COCH_3$	170.4		170.4			

[a] All carbon and proton resonances were assigned on the basis of 2D NMR (DQF-COSY, HSQC, HMBC and ROESY) experiments.
[b] Signal patterns are unclear due to overlapping.

1 but slightly differ from it in terms of the hydroxycinnamoyl residue. In the ^{1}H NMR spectrum of **3**, in addition to two characteristic doublets of olefinic protons at δ_H 6.32 and 7.50 ($J_{AX} = 15.9$ Hz), four aromatic protons as an AA′BB′ system at δ_H 7.49 (d, $J = 8.5$ Hz, H-2⁗/6⁗) and 6.79 (d, $J = 8.5$ Hz, 3⁗/5⁗) were observed. This data indicated that compound **3** contained *trans*-coumaroyl instead of *trans*-caffeoyl as an acyl ester moiety (Klimek, 1988). These conclusions were also confirmed by 2D NMR experiments (COSY, HSQC and HMBC). Consequently, the structure of compound **2** was established as chrysoeriol 7-*O*-[2‴-*O*-caffeoyl-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside] and named ozturkoside B, whereas structure of compound **3** was established as chrysoeriol 7-*O*-[2‴-*O*-*p*-coumaroyl- 6‴-*O*-acetyl-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside] and named ozturkoside C.

Compounds **4**–**11** were identified as verbascoside **4** (Sticher and Lahloub, 1982; Calis et al., 1984), leucoseptoside A **5** (Miyase et al., 1982) martynoside **6** (Miyase et al., 1982; Calis et al., 1984), 7-epicandicandiol **7** (Gonzales et al., 1981), linearol **8** , sidol **9** (Gonzales et al., 1981; Baser et al., 1996), sideroxol **10** (Baser et al., 1996; Topcu et al., 2002) epoxyisolinearol **11** (Venturella et al., 1975), respectively. The NMR and MS data of the known compounds were consistent with those previously reported.

3. Experimental

3.1. General

VLC: Silicagel 60, 63–200 μm (Merck). CC: Silicagel 60, 63–200 μm (Merck), Polyamide (Polyvinyl-polypyrrolidone) (Woelm), MPLC: Büchi B-681 glass column packed with LiChroprep RP-18 (Merck) using Lewa M5 peristaltic pump. TLC: Silicagel 60 F_{254} precoated aluminium plates (0.2 mm, Merck), Silicagel 60 F_{254} precoated glass plates (0.25 mm, Merck). Detection: UV flourescence and spraying 1% vanillin/H_2SO_4, followed by heating at 105 °C for 1–2 min. IR spectra: FT-IR spectrometer Perkin–Elmer 1720 X. UV spectra: Shimadzu UV-160 A. Negative mode ESI-MS: Varian MAT 731 (EI, 70 eV). FT-ESI-MS: Bruker APEX III MS. ^{1}H NMR, ^{13}C NMR, DEPT-135, ^{1}H–^{1}H COSY, ^{13}C–^{1}H HSQC, ^{13}C–^{1}H HMBC and ^{1}H–^{1}H ROESY spectra: Bruker AMX 300, DRX 500, DRX 600. Chemical shifts δ were given in ppm and coupling constants J in Hz. The spectra were measured in DMSO-d_6 for new compounds, CD_3OD for phenylethanoids and $CDCl_3$ for diterpenoids. The spectra were referenced against residual non-deuterated solvent.

3.2. Plant material

Sideritis ozturkii Aytac & Aksoy was collected from Konya, Derebucak in Southern Anatolia, Turkey, in July 2000. The voucher specimens (HUEF 00281) have been deposited at the Herbarium of the Department of Pharmacognosy, Faculty of Pharmacy, Hacettepe University, Ankara, Turkey.

3.3. Extraction and isolation

The air-dried and powdered aerial parts of *S. ozturkii* (500 g) were extracted with acetone (2500 ml × 2) at room temperature. The combined acetone extracts were dried in vacuo at 40 °C. The total extract (30 g) was initially fractionated by vacuum liquid chromatography (VLC) on silicagel (petroleum → → MeOH) to give eight main fractions (A–H). Fraction G was chromatographed on polyamide CC (H_2O → MeOH). Subfraction G8 which is rich in flavonoids were subjected to MPLC (MeOH: H_2O 20:80 → 50:50) affording compound 1 (25 mg), compound 2 (22 mg), compound 3 (55 mg). Subfraction G2 was separated by MPLC (MeOH:acetonitrile:H_2O 35:5:60) and then by silicagel CC ($CHCl_3$:MeOH:H_2O 90:10:1 → 80:20:2) to give compound 5 (8 mg), and compound 6 (6 mg). Subfraction G4 was also identified as compound 4 (382 mg). Compound 7 (8 mg), compound 8 (32 mg), compound 9 (20 mg), compound 10 (28 mg), and compound 11 (23 mg) were purified by Silica gel CC (cyclohexane: acetone:ethylmethylketone 90:10:0 → 80:15:5) from fraction D.

3.4. Ozturkoside A (*1*)

Amorphous yellow powder (MeOH); UV λ_{max} nm (MeOH): 250(sh), 270, 337; (NaOMe): 265, 396; ($AlCl_3$): 264, 297 (sh), 367 (sh), 390; ($AlCl_3$ + HCl): 278, 297 (sh), 352 (sh), 386 (NaOAc): 271, 346, 412 (sh); (NaOAc + H_3BO_3): 268, 345; IR ν_{max} (KBr) cm^{-1}: 3353 (OH), 1715 (est. C=O), 1657 (γ-pyrone C=O), 1602, 1516 (arom. ring); ^{1}H NMR (600 MHz; DMSO-d_6) (see Table 1); ^{13}C NMR (150 MHz; DMSO-d_6) (see Table 1); ESI-MS (m/z) negative ion mode: 827 $[M-H]^-$, $C_{39}H_{40}O_{20}$. FT-ESI-MS (m/z): 851.20368 $[M+Na]^+$, $C_{39}H_{40}O_{20}Na$ (calc. 851.20105).

3.5. Ozturkoside B (*2*)

Amorphous yellow powder (MeOH); UV λ_{max} nm (MeOH): 250 (sh), 270, 336; (NaOMe): 260, 392; ($AlCl_3$): 263, 298 (sh),368 (sh), 389; ($AlCl_3$ + HCl): 278, 297 (sh), 353 (sh), 385; (NaOAc): 270, 345, 412 (sh); (NaOAc + H_3BO_3): 269, 345; IR ν_{max} (KBr) cm^{-1}: 3399 (OH), 1714 (est. C=O), 1659 (γ-pyrone C=O), 1597, 1499 (arom. ring); ^{1}H NMR (500 MHz; DMSO-d_6) (see Table 1); ^{13}C NMR (125 MHz; DMSO-d_6) (see Table 1); ESI-MS (m/z) negative ion mode: 785 $[M-H]^-$, $C_{37}H_{38}O_{19}$. FT-ESI-MS (m/z): 809.19169 $[M+Na]^+$, $C_{37}H_{38}O_{19}Na$ (calc. 809.19048).

3.6. Ozturkoside C (*3*)

Amorphous yellow powder (MeOH); UV λ_{max} nm (MeOH): 250 (sh), 271, 336; (NaOMe): 265, 392; ($AlCl_3$): 264, 297 (sh), 368 (sh), 389; ($AlCl_3$ + HCl): 278, 296 (sh), 353 (sh), 386; (NaOAc): 271, 347, 412 (sh); (NaOAc + H_3BO_3): 270, 346; IR ν_{max} (KBr) cm^{-1}: 3396 (OH), 1714 (est. C=O), 1661 (γ-pyrone C=O), 1604, 1515 (arom. ring); ^{1}H NMR (300 MHz; DMSO-d_6) (see Table 1); ^{13}C NMR (75 MHz; DMSO-d_6) (see Table 1); ESI-MS (m/z) negative ion mode: 811 $[M-H]^-$, $C_{39}H_{40}O_{19}$. FT-ESI-MS (m/z): 835.21183 $[M+Na]^+$, $C_{39}H_{40}O_{19}Na$ (calc. 835.20613).

3.7. Verbascoside (**4**)

Amorphous yellow powder (MeOH); UV λ_{max} nm (MeOH): 220, 234 (sh), 290, 329; IR ν_{max} (KBr) cm^{-1}: 3392, 1699, 1631, 1604, 1523.

3.8. Leucoseptoside A (**5**)

Amorphous yellow powder (MeOH); UV λ_{max} nm (MeOH): 219, 234 (sh), 289, 327; IR ν_{max} (KBr) cm^{-1}: 3380, 1700, 1632, 1599, 1516.

3.9. Martynoside (**6**)

Amorphous yellow powder (MeOH); UV λ_{max} nm (MeOH): 219, 234 (sh), 288, 327; IR ν_{max} (KBr) cm^{-1}: 3399, 1700, 1634, 1595, 1516.

3.10. 7-Epicandicandiol (**7**)

Colorless needles ($CHCl_3$); UV λ_{max} nm ($CHCl_3$): 248; IR ν_{max} (KBr) cm^{-1}: 3390, 2929, 1646, 871; EI-MS (m/z): 304.3 $[M]^+$, 286.3 $[M-H_2O]^+$, 271.2 $[M-H_2O-CH_3]^+$, $C_{20}H_{32}O_2$.

3.11. Linearol (**8**)

Colorless prisms ($CHCl_3$); UV λ_{max} nm ($CHCl_3$): 247,5; IR ν_{max} (KBr) cm^{-1}: 3462, 2930, 1655, 875, 1715; EI-MS (m/z): 362.3 $[M]^+$, 344.3 $[M-H_2O]^+$, 326.3 $[M-2H_2O]^+$, $C_{22}H_{34}O_4$.

3.12. Sidol (**9**)

White resin ($CHCl_3$); UV λ_{max} nm ($CHCl_3$): 247,5; IR ν_{max} (KBr) cm^{-1}: 3462, 2930, 1655, 875, 1715; ESI-MS (m/z) positive ion mode: 385.2 $[M+Na]^+$, $C_{22}H_{34}O_4$.

3.13. Sideroxol (**10**)

White resin ($CHCl_3$); UV λ_{max} nm ($CHCl_3$): 248; IR ν_{max} (KBr) cm^{-1}: 3432, 2927, 1043; ESI-MS (m/z) positive ion mode: 343.2 $[M+Na]^+$, $C_{20}H_{32}O_3$.

3.14. Epoxyisolinearol (**11**)

White resin ($CHCl_3$); UV λ_{max} nm ($CHCl_3$): 247,5; IR ν_{max} (KBr) cm^{-1}: 3432, 2927, 1043, 1730; EI-MS (m/z): 378.3 $[M]^+$, 396.3 $[M+H_2O]^+$, $C_{22}H_{34}O_5$.

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