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Two benzophenone *O*-arabinosides and a chromone from *Hypericum annulatum*

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Abstract

Two benzophenone *O*-arabinosides, annulatophenonoside (**1**) and acetylannulatophenonoside (**2**) were isolated from the methanol extract of the herb of *Hypericum annulatum*. The structures of the benzophenones were established as 2-*O*-α-L-arabinofuranosyl-3′,5′,6-trihydroxy-4-methoxybenzophenone (**1**) and 2-*O*-α-L-3″-acetylarabinofuranosyl-3′,5′,6-trihydroxy-4-methoxybenzophenone (**2**) based on spectral and chemical evidence. A chromone, 5,7-dihydroxy-3-methylchromone (**3**) was isolated from the chloroform extract. Although it has been previously synthesized it is encountered in a plant source for the first time. Co-occurrence of the two new benzophenone *O*-arabinosides along with the biogenetically related 1,5,7-trihydroxy-3-methoxyxanthone was not found.

Keywords: *Hypericum annulatum*; Guttiferae; Benzophenone *O*-arabinosides; Annulatophenonoside; Acetylannulatophenonoside; 5,7-Dihydroxy-3-methylchromone

1. Introduction

Benzophenone *O*-glycosides are encountered rarely in plants. Up to date only two compounds, 2-*O*-β-D-glucopyranosyl-4′,6-dihydroxy-4-methoxybenzophenone found in *Gnidia involucrata* (Ferrari et al., 2000) and 2′-*O*-β-D-glucopyranosyl-2,4,5′,6-tetrahydroxybenzophenone (hypericophenonoside) isolated from *Hypericum annulatum* (Kitanov and Nedialkov, 2001) have been reported. In the latter species hypericophenonoside occurs together with a large amount of 1,3,7-trihydroxyxanthone (gentisein) and their biogenic relationship was demonstrated (Kitanov and Nedialkov, 2001). This investigation was undertaken to establish other biogenic relationships between benzophenone *O*-glycosides and xanthones and led to the isolation and identification of a new benzophenone *O*-arabinoside, its acetyl derivative and a 3-methylchromone.

2. Results and discussion

An extensive chromatographic procedure of EtOAc extract starting with CC on polyamide (H_2O–20% EtOH) followed by CC on silica gel (C_6H_6–Me_2CO mixtures) led to the isolation of two benzophenone *O*-arabinosides. After acid hydrolysis both compounds gave 2,3′5′,6-tetrahydroxy-4-methoxybenzophenone (annulatophenone) as an aglycone. The aglycone was identified by UV, IR, EI–MS, ^{1}H NMR spectra and co-TLC and it was previously reported for this species (Kitanov and Nedialkov, 2001). 3-Methylchromone was isolated from $CHCl_3$ extract using a CC on silica gel and C_6H_6–EtOH (98:2) as an eluent. The fraction containing this compound was subjected to flash chromatography on silica gel ($CHCl_3$–MeOH 95:5). Sephadex LH-20 (MeOH) and recrystalization were used as a final purification step.

Compound **1** was easily dissolved in water and gave a dark brown color with ferric chloride. The IR spectrum of **1** showed absorption bands at 3222–3343 (OH); 1634 (C=O); 1626, 1584 (C=C) cm^{-1}. The bathochromic shift of the band at 301 nm in the UV spectrum with $AlCl_3$ (+39) revealed the presence of free hydroxyl *ortho* to the carbonyl. The HREI–MS of **1** showed the highest peak at *m*/*z* 276.06327 (rel. int. 100%) corresponding to the

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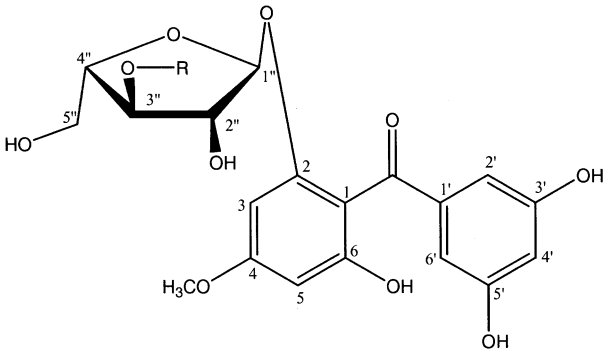

1, R = H
2, R= CH_3CO

Fig. 1. Structures of annulatophenonoside (**1**) and acetylannulatophenonoside (**2**).

molecular formula $C_{14}H_{12}O_6$ of annulatophenone. The FAB–MS spectrum presented the $[M+H]^+$ peak at *m/z* 409 consistent with molecular formula $C_{19}H_{20}O_{10}$ and the base peak at *m/z* 277 $[M_{agl}+H]^+$ indicating aglycone moiety. The molecular mass of **1** was also confirmed by elemental analysis data: C 55.28 and H 4.82% respectively.

The ^1H NMR spectrum of **1** in acetone-d_6 (Table 1) showed the presence of signals from one chelated hydroxyl proton at δ 10.72 and a broad peak at δ 8.50 (2H). Both disappear after addition of D_2O. The signals of three protons of ring B in compound **1**, a triplet at δ 6.52 (1H, $J=2.2$ Hz) and a doublet at δ 6.63 (2H, $J=2.2$ Hz), have the same shape and position as the analogous protons of the aglycone (Kitanov and Nedialkov, 2001). The symmetry of ring A was broken by attaching of arabinosyl moiety to position 2 of annulatophenone, which was shown by two doublets at δ 6.32 (1H, $J=2.3$ Hz) and 6.21 (1H, $J=2.3$ Hz). This fact unambiguously points to C-2 as the linkage position of arabinose.

The doublet at δ 5.45 (1H, $J=1.6$ Hz) and multiplets at δ 3.59–3.77 and 3.88–3.95 were assigned to the arabinosyl residue with α-configuration of anomeric proton. Signals corresponding to 5 sugar carbons (δ 108.25, 83.14, 78.44, 87.32, 62.8) are typical for arabinofuranosides (Ritchie at al., 1975). The assignment of the signals was confirmed by ^1H–^1H COSY, ^{13}C NMR and HETCOR. Multiplicities were revealed by DEPT experiments. Finally, compound **1** was identified as 2-*O*-α-L-arabinofuranosyl- 3′,5′,6-trihydroxy-4-methoxybenzophenone, named annulatophenonoside (Fig. 1).

Compound **2** was isolated as colorless prisms. The molecular formula $C_{21}H_{22}O_{11}$ of this component was determined on the basis of FAB–MS data, elemental analysis and ^1H and ^{13}C NMR results. Its UV spectra were identical with that of compound **1**, suggesting little difference between the two structures. The IR spectrum of **2** showed absorption bands at 3205–3425 (chelated OH), 1732–1747 (ester >C=O), 1620 (>C=O), 1585, 1506 (>C=C<, aromatic) cm^{-1}. The HREI–MS of **2** showed the highest peak at *m/z* 276.06449 corresponding to the molecular formula $C_{14}H_{12}O_6$ of 2,3′,5′,6-

Table 1
^1H- and ^{13}C NMR spectral data for compounds **1** and **2** (CD_3CO)[a]

Carbon number	**1**		**2**	
	^1H (δ) *J* (Hz)	^{13}C (δ)	^1H (δ) *J* (Hz)	^{13}C (δ)
1	–	109,41	–	109,5
2	–	159,79	–	159.72[b]
3	6.32 (*d*, 2.3)	95,68	6.33 (*d*, 2.3)	95,53
4	–	166,29	–	166,42
5	6.21 (*d*, 2.3)	96,13	6.22 (*d*, 2.3)	96,24
6	10.72 (*br. s*, OH)	163,68	10.77 (*br. s*, OH)	163,98
1′	–	144,34	–	144,57
2′	6.63 (*d*, 2.2)[b]	108.35[b]	6.62 (*d*, 2.2)[b]	108.17[b]
3′	8.50 (*br.s*, OH)[b]	159.66[b]	8.51 (*br.s*, OH)[b]	159,72[b]
4′	6.52 (*t*, 2.2)	107,54	6.51 (*t*, 2.2)	107,25
5′	8.50 (*br. s*, OH)[b]	159.66[b]	8.51 (*br. s*, OH)[b]	159,72[b]
6′	6.63 (*d*, 2.2)[b]	108.35[b]	6.62 (*d*, 2.2)[b]	108.17[b]
1″	5.45 (*d*, 1.6)	108,25	5.51 (*s*)	108,36
2″	3.59-3.77 (*m*)[c]	83,14	3.55 (*d*, 1.2)	80,49
3″	3.88-3.95 (*m*)[c]	78,44	4.77 (*dd*, 1.2, 3.6)	80,59
4″	3.88-3.95 (*m*)[c]	87,32	4.06 (*dd*, 3.6, 3.7)	86,58
5″	3.59-3.77 (*m*)[c]	62,8	3.71 (*t*, 3.7)	63,03
OCH_3	3.84 (*s*)	56,63	3.86 (*s*)	56,69
C=O	–	198,96	–	198,94
CH_3 (AcO)	–	–	1.96 (*s*)	21,38
C=O (AcO)	–	–	–	171,65

[a] All signals were assigned by ^1H–^1H-COSY, HETCOR and DEPT experiments.
[b] Overlapping.
[c] Signal patterns were unclear due to overlapping.

tetrahydroxy-4-methoxybenzophenone (annulatophenone). The FAB–MS spectrum presented the $[M+H]^+$ peak at m/z 451 consistent with molecular formula $C_{21}H_{22}O_{11}$ and the base peak at m/z 277 $[M_{agl}+H]^+$ indicating the aglycone moiety.

The ^{1}H NMR spectrum of **2** recorded in acetone-d_6 (Table 1) showed the presence of a singlet (3H) at δ 1.96 originated from methyl group in acetyl moiety. The signals of the sugar protons in ^{1}H NMR were well resolved. The chemical shift at δ 4.77 (1H, *dd*, $J_{2''-3''}=1.2$ Hz, $J_{3''-4''}=3.6$ Hz) was attributed to H-3″ and it appeared ca 1 ppm downfield compared to that of compound **1**. This is due to the deshielding effect of the nearby attached acetyl moiety. The comparison of ^{13}C NMR spectral data with that of compound **1** (Table 1) showed 2.15 ppm downfield shift of C-3″ signal and 2.65 and 0.74 upfield shift of C-2″ and C-4″ signals, respectively (Markham and Chari, 1982). This evidence unambiguously confirmed C-3″ as a linkage position of acetyl moiety. The signals of the other sugar protons appeared at δ 3.55 (1H, *d*, $J_{2''-3''}=1.2$ Hz, H-2″), 3.71 (2H, *t*, $J_{4''-5''}=3.7$ Hz, H-5″) and 4.06 (1H, *dd*, $J_{3''-4''}=3.6$ Hz, $J_{4''-5''}=3.7$ Hz, H-4″) were less affected by acetylation. The singlet at δ 5.51 was attributed to anomeric proton in arabinose moiety and suggesting its α-configuration.

The signals at δ 3.86 (3H, *s*, CH_3O), 6.22 (1H, *d*, $J_{3-5}=2.3$ Hz, H-5), 6.33 (1H, *d*, $J_{3-5}=2.3$ Hz, H-3), 6.62 (2H, *d*, $J_{2',6'-4'}=2.2$ Hz, H-2′ and H-6′) and 6.51 (1H, *t*, $J_{2',6'-4'}=2.2$ Hz, H-4′) were attributable to the aglycone moiety and have similar pattern to that of compound **1**. Multiplicities were revealed by a DEPT experiment and complete attribution was performed by ^{1}H–^{1}H COSY and HETCOR. Thus, compound **2** is 2-*O*-α-L-3″-acetylarabinofuranosyl-3′,5′,6-trihydroxy-4-methoxybenzophenone, named acetylannulatophenonoside (Fig. 1). Both identified compounds **1** and **2** are new natural products.

In a previous paper we reported a spontaneous transformation of 2′-*O*-β-D-glucopyranosyl-2,4,5′,6-tetrahydroxybenzophenone (hypericophenonoside) to 1,3,7-trihydroxyxanthone (gentisein) upon acid and enzymatic hydrolysis of the glucoside (Kitanov and Nedialkov, 2001). This led to dehydration and cyclization of the 2,2′-hydroxyls from ring A and B of the benzophenone aglycone. Both hypericophenonoside an gentisein were present in large amounts in the herb of *Hypericum annulatum* (Kitanov and Nedialkov, 2001).

We studied whether or not transformation of annulatophenonoside **1** and acetylannulatophenonoside **2** to the corresponding 1,5,7-trihydroxy-3-methoxyxanthone occurred. The possible mechanism of such transformation is hydrolysis of compounds **1** and **2** and subsequent oxidative coupling of the resultant aglycone leading to the related xanthone. The EtOAc and $CHCl_3$ extracts were investigated for occurrence of 1,5,7-trihydroxy-3-methoxyxanthone, but it was not found in both of them. Thus, this oxidative biosynthetic pathway to xanthone formation from benzophenone *O*-glycosides appears not to occur in *Hypericum annulatum*.

Compound **3** was isolated from the $CHCl_3$ extract and was identified by means of mp, elemental analysis, UV, IR, EI–MS, ^{1}H and ^{13}C NMR data as 5,7-dihydroxy-3-methylchromone. This chromone was previously synthesized by Jain and co-workers (Jain et al., 1989). This compound was encountered in a plant source for the first time.

3. Experimental

3.1. General experimental procedures

Mps uncorr. OR was measured on a Perkin-Elmer 241 polarimeter using MeOH as a solvent. UV spectra were run in MeOH and shift reagents on a Specord UV-vis and IR spectra were recorded in nujol on a Shimadzu FTIR-8101 M instrument. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker ARX 300 apparatus at 300 an 75 MHz, respectively, in acetone-d_6, using TMS as an internal standard. HREI- and FAB–MS analyses were performed on a Varian MAT 711 mass spectrometer at 70 eV in positive ion mode and thermospray MS (TSP–MS) was registered on a LC/MS HP 5989 A Hewlett Packard instrument. Open column chromatography (CC): polyamide S (Woelm, Germany), silica gel 60 (63–200 and 40–63 μm) (Merck, Germany) and Sephadex LH-20 (Pharmacia, Sweden). TLC was performed using silica gel 60 F_{254} (Merck, Germany), $CHCl_3$–MeOH–H_2O (70:20:2) (A), $CHCl_3$–AcOH (98:2) (B), EtOAc–MeOH–H_2O–AcOH (65:15:15:20) (C) and cellulose (Merck, Germany), EtOAc–Pyridine–H_2O (12:5:4) (D) mixtures were used as solvents. Acid hydrolysis was carried out with HCl (100 °C, 2 h). Detection of benzophenones was by spraying with Fast blue salt B (Riedel-De Haën, Gemany) in MeOH–H_2O (1:1), chromone by 1% Naturstoffreagenz A (Roth, Germany) in MeOH and sugars by anizidine phtalate reagent followed by heating at 110 °C for 3–5 min.

3.2. Plant material

The aerial parts of *Hypericum annulaum* (syn. *H. degenii*) were collected during the flowering season from wild habitat at the Central Rodope Mountains in July 1997. A voucher specimen (No. 144296) has been deposited at the Herbarium of Botany Institute of Sofia (SOM).

3.3. Extraction and isolation

The air-dried and powdered aerial parts (1.7 kg) were deffated with *n*-hexane (1 l×6) and extracted with MeOH (6 l×8). The crude MeOH residue was dissolved

in hot H_2O (2 l), filtered and treated with $CHCl_3$ (300 ml×10). The aq. phase was fractionated with EtOAc (500 ml×7). The EtOAc fraction (52 g) was chromatographed on a polyamide column (150 g), using a 0–20% EtOH linear gradient and gave mixture of **1** and **2**. The mixture was separated by means of column chromatography over silica gel (step gradient C_6H_6–Me_2CO 7:3–5:5). Subsequent Sephadex LH-20 gel filtration (MeOH) and recrystallization from H_2O–EtOH gave pure compounds **1** (1.97 g) and **2** (3.5 g). The $CHCl_3$ extract (36 g) was subjected to CC over silica gel (63–200 μm) and eluted with $C_6H_6 \rightarrow C_6H_6$–EtOH (90:10) step gradient. The fraction eluted with C_6H_6–EtOH (98:2) was then separated from the accompanied compounds by flash chromatography over silica gel (40–63 μm), using $CHCl_3$–MeOH (95:5) as a mobile phase. Sephadex LH-20 gel filtration (MeOH) and recrystallization from MeOH–C_6H_6 were used as a final purification step to give 110 mg of compound **3**.

3.4. Acid hydrolysis of *1* and *2*

Samples of compounds **1** and **2** (50 mg) were dissolved in 10 ml 1 N HCl and refluxed on water bath (100 °C). The hydrolysis was monitored by a TLC, system A, time interval 5–10 min, for 2 h, after dilution with H_2O and cooling, the aglycone ppt. was filtered and recrystallized from H_2O–EtOH. The aq. solution was evapd. to dryness in vacuo. The residue was dissolved in 50% EtOH and examined for sugar by TLC using solvent systems C and D. The aglycone of compounds **1** and **2** was identified as 2,3′,5′,6-tetrahydroxy-4-methoxybenzophenone on the basis of co-TLC, UV, IR, EI–MS and ^{1}H NMR and the sugar was identified to be L-arabinose.

3.5. Annulatophenonoside (*1*) (1.97 g)

Yellow crystalloid mass (from H_2O–EtOH), mp 162–164 °C. $[\alpha]_D^{20}$ −79.52° (MeOH, *c* 1.0550). UV λ_{max}^{MeOH} nm (log ε): 209 (4.63), 220 *sh*, 282 (4.17), 301 (4.17); + $AlCl_3$ 209, 227 *sh*, 312 *sh*, 340; + $AlCl_3$/HCl 222 *sh*, 298 *sh*, 325; + NaOAc 281, 300; + NaOAc/H_3BO_3 280, 300. IR ν_{max}^{nujol} cm^{-1}: 3222–3343 (chelated OH); 1634 (>C=O); 1626, 1584 (>C=C<, aromatic). ^{1}H and ^{13}C NMR: see Table 1. HREI–MS *m/z* (rel. int.): 276.06327 $[M_{agl}]^{+\cdot}$ $[C_{14}H_{12}O_6]$ (100) (calc. 276.241). FAB–MS *m/z* (rel. int.): 409 $[M+H]^+$ (28), 277 $[M_{agl}+H]^+$ (100), 259 $[M_{agl}\text{-}OH+H]^+$ (14), 167 $[M_{agl}\text{-}109]^+$ (15), 137 $[M_{agl}\text{-}139]^+$ (10), 133 $[(M_{sugar}–H_2O)+H]^+$ (13). Found: C, 55.28; H, 4.82% $C_{19}H_{20}O_{10}$ requires: C, 55.88; H, 4.94%.

3.6. Acetylannulatophenonoside (*2*) (3.5 g)

Colorless prismatic crystals (from H_2O–EtOH), mp 177.5–179.5 °C. $[\alpha]_D^{20}$ −7.48° (MeOH, *c* 1.0150). UV λ_{max}^{MeOH} nm (log ε): 207 (4.812), 221 *sh*, 280 (4.182), 303 (4.182); + $AlCl_3$ 207, 222 *sh*, 312 *sh*, 340; + $AlCl_3$/HCl 207, 222 *sh*, 280 *sh*, 324; + NaOAc 278, 300; + NaOAc/H_3BO_3 284*sh*, 306. IR ν_{max}^{nujol} cm^{-1}: 3205–3425 (chelated OH), 1732–1747 (>C=O, ester), 1620 (>C=O), 1585, 1506 (>C=C<, aromatic). ^{1}H and ^{13}C NMR: see Table 1. HREI–MS *m/z* (rel. int.): 276.06449 $[M_{agl}]^{+\cdot}$ $[C_{14}H_{12}O_6]$ (100) (calc. 276.241), 43 $[CH_3CO]^+$ (85). FAB-MS *m*/z (rel. int.): 451 $[M+H]^+$ (38), 277 $[M_{agl}+H]^+$ (100), 137 $[M_{agl}\text{-}139]^+$ (6). Found: C, 55.78; H, 4.90% $C_{21}H_{22}O_{11}$ requires: C, 56.00; H, 4.92%.

3.7. 5,7-Dihydroxy-3-methylchromone (*3*) (110 mg)

Pale yellow needles (from MeOH–C_6H_6), mp 217–218 °C. UV λ_{max}^{MeOH} nm (log ε): 208 (4.41), 229 (4.25), 252 (4.32), 259 (4.37), 296 (3.98), 320 *sh*; + $AlCl_3$ 226 *sh*, 265, 309, 373; + $AlCl_3$/HCl 226 *sh*, 265, 308, 373; + NaOMe 221 *sh*, 262, 323; + NaOAc 265, 326; + NaOAc/H_3BO_3 252, 259, 297. IR ν_{max}^{nujol} cm^{-1}: 3300 (chelated OH); 1660 (>C=O); 1620, 1587 (>C=C<, aromatic). ^{1}H NMR (300 MHz, acetone-d_6): δ 12.85 (1H, *s*, 5-OH), 9.51 (1H, *br. s*, 7-OH), 7.92 (1H, *d*, *J* = 1.1, H-2), 6.31 (1H, *d*, *J* = 20, H-8), 6.22 (1H, *d*, *J* = 2.0, H-6), 1.90 (3H, *d*, *J* = 1.1, 3-CH_3). ^{13}C-NMR (75 MHz, acetone-d_6): δ 183.53 (>C=O), 165.40 (C-7), 164.01 (C-5), 160.06 (C-9), 154.30 (C-2), 120.12 (C-3), 106.25 (C-10), 100.22 (C-6), 95.02 (C-8), 10.82 (3-CH_3). EI–MS (probe), 70 eV, *m/z* (rel. int.): 192 $[M]^+$ (100), 163 (38), 152 (15), 137 (12), 124 (70), 118 (12), 96 (14), 69 (32). Found: C, 62.37; H, 4.01% $C_{10}H_8O_4$ requires: C, 62.50; H, 4.20%.

3.8. Acetylation of *3*

Compound **3** (23.8 mg) was treated with C_5H_5N (0.6 ml) and Ac_2O (1 ml) and refluxed for 3 h. The reaction mixture was poured on ice and kept at 4 °C for 24 h. The ppt. was filtered, dried and crystallized from EtOH to give 18.3 mg of **3**-diacetate derivative **3a**.

3.9. 5,7-Diacetyl-3-methylchromone (*3a*) (18.3 mg)

Colorless prisms (from EtOH), mp 146.5–148 °C. IR ν_{max}^{nujol} cm^{-1}: 2369 (–CH_3), 1770 (>C=O, ester), 1653 (>C=O), 1622, 1574 (>C=C<, aromatic). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (1H, *d*, *J* = 1.2 Hz, H-2), 7.18 (1H, *d*, *J* = 2.3 Hz, H-8), 6.81 (1H, *d*, *J* = 2.3 Hz, H-6), 2.44 (3H, *s*, 5-OAc), 2.33 (3H, *s*, 7-OAc), 1.96 (3H, *d*, *J* = 1.2 Hz, 3-CH_3). EI–MS (probe) 70 eV, *m/z* (rel. int.): 276 $[M]^+$ (0.1); 234 $[M–OAc]^+$ (22), 192 $[M–2OAc]^+$ (60), 163 (12), 43 $[CH_3CO]^+$ (100). TSP–MS *m/z* (rel. int.): $[M+H]^+$ 277 (64), 235 $[M–OAc–H]^+$ (100), 193 $[M–2OAc+H]^+$ (44).

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