

## BENZOFURAN DERIVATIVES FROM *ENCELIOPSIS COVILLEI*

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**Key Word Index**—*Enceliopsis covillei*; Asteraceae; benzofuran derivatives; structure elucidation.

**Abstract**—Phytochemical analyses of the leaves of *Enceliopsis covillei* afforded several benzofuran derivatives, two of them being new compounds. The unusual structure of one of those comprises an acetyl group at C-2 of the furan ring.

### INTRODUCTION

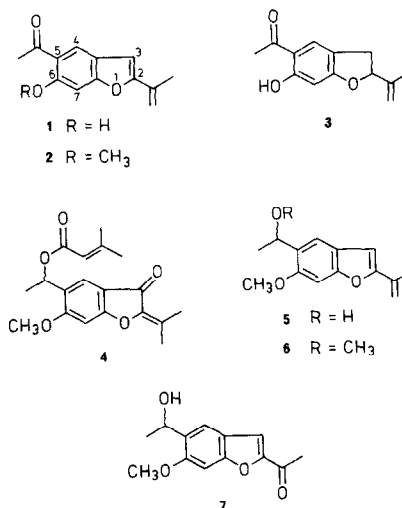
*Enceliopsis* (Gray) A. Nels. (tribe Heliantheae) is a genus of five herbaceous perennial taxa found primarily in the Great Basin desert of the southwestern USA [1, 2]. This genus, along with the related genera *Encelia*, *Geraea* and *Flourensia*, has proven to be a rich source of benzofuran and chromene (benzopyran) derivatives [3–10]. In previous work on the phytochemistry of *Enceliopsis* we showed that numerous benzofurans are accumulated in this genus [9, 10]. As part of our investigations on this group of genera we have studied *Enceliopsis covillei* (A. Nels.) S. F. Blake and wish to report on the benzofurans isolated from this species.

### RESULTS AND DISCUSSION

The presence of lipophilic aromatic compounds in the leaves of *Enceliopsis covillei* was first indicated by several orange, yellow and blue fluorescing spots (visible under UV<sub>366</sub> nm) after TLC of the dichloromethane extract. Co-chromatography with authentic standards revealed the presence of the benzofuran derivatives 1–4. Whereas compounds 1–3 have already been isolated from many genera of the Asteraceae [5] the ester 4 was so far only known from *Enceliopsis argophylla* [9]. Of the three additional compounds 5 proved to be 2-isopropylene-5-(1ξ-hydroxyethyl)-6-methoxybenzofuran recently isolated from *Oxylobus adscendens* [11]. The spectral data obtained were identical to those published for this compound. Compound 6 is the methyl ether of 5 as indicated by the mass spectrum and <sup>1</sup>H NMR data (Table 1). The mass of the molecular ion of 6 was 14 units higher than that of 5 and their mass spectra showed an analogous fragmentation pattern differing only in the loss of water (5) and of methanol (6), respectively, from [M]<sup>+</sup>. The <sup>1</sup>H NMR data also proved to be identical with the exception that a second methoxyl signal at δ3.7 was

present in the spectrum of 6. From these data the structure of 2-isopropylene-5-(1ξ-methoxyethyl)-6-methoxybenzofuran could be deduced for this new natural product. Compound 7 proved also to be a novel benzofuran derivative. The <sup>1</sup>H NMR spectrum of this compound showed signals indicative of a 2-acetylbenzofuran (Table 1). The signal of the furan C-3 proton at δ7.7 suffered a large downfield shift with respect to 2-isopropylene benzofurans (e.g. 6, δ6.6, H-3) due to the acetyl substituent (δ2.5) at C-2. The signals of the aromatic protons at C-4 and C-7 appeared at δ7.5 and 7.0, respectively. The remaining signals in the <sup>1</sup>H NMR spectrum can be accounted for by the substituents MeOAr (δ3.9) and MeCHOHAr (δ1.5 d; δ5.1 q).

The pattern of benzofuran constituents was found not to vary when five different collections of *Enceliopsis covillei* were compared by TLC. 2-Acetylbenzofurans are found very rarely in the Asteraceae family [5]. Thus, it is interesting to note from a chemosystematic standpoint that several such unusual compounds have been isolated earlier from species of *Encelia* [12, 13] and from



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Table 1.  $^1\text{H}$  NMR data of compounds **6** and **7** [multiplicity,  $\delta$  (ppm),  $J$  (Hz), coupling group] (integration confirms the number of H present in the various functionalities listed below)

	<b>6</b>	<b>7</b>
H-3	s 6.6	s 7.7
H-4	s 7.5	s 7.5
H-7	s 7.0	s 7.0
MeOAr	s 3.9	s 3.9
MeO	s 3.7	
MeCHOHAr	q 5.1 (6.5, Me)	q 5.2 (6.5, Me)
MeCHOHAr	d 1.5 (6.5, CH)	d 1.5 (6.5, CH)
MeCCH <sub>2</sub>	s (br) 5.7 (5.1)	
MeCCH <sub>2</sub>	S (br) 2.1	
MeCO		s 2.5

*Enceliopsis* [10] and may be encountered rather frequently in this group of genera. Also the co-occurrence of unusual benzofuran esters like compound **4** in *Enceliopsis covillei* and *Enceliopsis argophylla* might provide information with regard to a possible systematic close relationship of these two taxa.

#### EXPERIMENTAL

**Plant material and extraction.** *Enceliopsis covillei* (collection number 256) was collected in Inyo County, California, in April 1984, and identified by Professor Curtis Clark (California State University, Pomona). A voucher specimen was deposited at the herbarium of this University. The air dried leaves were ground and extracted with  $\text{CH}_2\text{Cl}_2$ . The extract was separated by CC on silica gel using  $\text{CH}_2\text{Cl}_2$  as an eluant and by CC on Sephadex LH-20 using MeOH as an eluant. Fractions containing 20 ml were monitored by TLC on silica gel, using  $\text{CH}_2\text{Cl}_2$ -MeOH (49:1) as an eluant. Detection of the benzofurans was achieved by their fluorescence on the TLC plate under UV at 366 nm.

**Spectroscopic methods.** UV: Contron Uvikon 810; solvent MeOH.  $^1\text{H}$  NMR: Varian EM 390 (90 MHz); solvent  $\text{CDCl}_3$ . GC/MS: Varian gas chromatograph 2700, BP1 wide bore capillary column, coupled with a Varian-MAT CH7-A mass spectrometer, electron impact 75 eV, with Data System SS 200.

**2-Isopropylene-5-(1- $\xi$ -methoxyethyl)-6-methoxybenzofuran (6).**

UV  $\lambda_{\text{max}}^{\text{MeOH}}$  nm: 283. For  $^1\text{H}$  NMR data see Table 1. MS  $m/z$  (rel. int.): 246  $[\text{M}]^+$  (18), 231  $[\text{M} - \text{Me}]^+$  (42), 214  $[\text{M} - \text{MeOH}]^+$  (100), 199  $[\text{M} - \text{Me}]^+$  (2), 171  $[\text{M} - \text{CO}]^+$  (70), 143 (52), 128 (95), 115 (32), 45 (64), 43 (48), 41 (81).

**2-Acetyl-5-(1- $\xi$ -hydroxyethyl)-6-methoxybenzofuran (7).** UV  $\lambda_{\text{max}}^{\text{MeOH}}$  nm: 325, 290 (sh), 252. For  $^1\text{H}$  NMR data see Table 1. MS  $m/z$  (rel. int.): 234  $[\text{M}]^+$  (3), 219  $[\text{M} - \text{Me}]^+$  (5), 216  $[\text{M} - \text{H}_2\text{O}]^+$  (16), 201  $[\text{M} - \text{Me}]^+$  (14), 189 (2), 173 (3), 145 (10), 131 (3), 115 (3), 102 (4), 91 (1), 89 (1), 79 (1), 77 (3), 76 (3), 75 (1), 69 (1), 63 (2), 62 (1), 51 (4), 50 (2), 44 (6), 43 (100).

Besides collection number 256 collections 233, 234, 255 and 257 (all from Inyo County, California) were screened for their leaf benzofurans by TLC on silica gel. Dates and localities of collections can be obtained from the authors.

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