Table 1. Selected UV and IR data of compounds 1–4

Compound	UV λ_{max} (nm)	IR ν_{max} (cm^{-1})
1	212, 250, 305, 354	3300, 1710, 1612
2	212, 250, 305, 353	3400, 1718, 1628, 1605
3	213, 251, 305, 355, 361	3440, 1685, 1630, 1615
4	212, 250, 305, 350	2950, 2840, 1740, 1625, 1610

phenolic OH), 9.9–10.96 (2 overlapping *br s*, 2H, phenolic OH).

Tri-O-methylwedelolactone (**4**). To **3** (30 mg) in MeOH was added excess Et_2O–CH_2N_2 and the mixture left overnight. Removal of the solvent and passage through a silica gel column using chloroform gave **4**, crystallized from MeOH to give needles, mp 247° (lit. mp 247° [1]) *m/z* 356 $[M]^+$. ^{1}H NMR: δ3.80, 3.90 (each *s*, each 3H, each OMe), 3.92 (*s*, 6H, 2 × OMe), 6.35, 6.54 (each *d*, each 1H, J = 2.5 Hz, H-6 or H-8) 7.15, 7.45 (each *s*, each 1H, H-10 or H-13).

Acknowledgements—We are grateful to Dr. B. C. Das, Institut du Chimie des Substances Naturelles, Gif-sur-Yvette and Dr. R. S. Kapil, CDRI, Lucknow, for the mass spectral data reported.

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Phytochemistry, Vol. 24, No. 12, pp. 3069–3071, 1985.
Printed in Great Britain.

0031–9422/85 $3.00 + 0.00

BENZOFURAN DERIVATIVES FROM TWO *ENCELIA* SPECIES

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(*Received* 28 *March* 1985)

Key Word Index—*Encelia actoni*; *E. virginensis*; Asteraceae; new benzofuran derivatives; 2-acetoxy-5-(1ξ-hydroxyethyl)-6-methoxybenzofuran; structure elucidation.

Abstract—From *Encelia actoni* and *E. virginensis* two new benzofuran esters could be isolated. The unusual structure of the skeleton comprises an acetyl group at C-2 of the furan ring.

INTRODUCTION

The genus *Encelia* Adans. (tribe Heliantheae) is a dominant element of the Mojave and Sonoran deserts from the southwest United States to Mexico and comprises some 20 taxa that are shrubby perennials [1]. Previously we showed that chromenes (benzopyrans) and benzofurans are characteristic for *Encelia* [2–6] as well as for the genera *Enceliopsis* (Gray) A. Nels. [7, 8] and Geraea Torr. & Gray [Mitsakos and Proksch, in preparation] which are considered to be closely related to *Encelia* [9]. In this study we wish to report the structure elucidation of two new benzofuran esters with unusual substitution from *E. actoni* and *E. virginensis*.

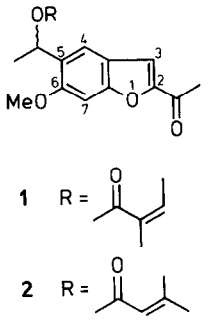
RESULTS AND DISCUSSION

The presence of lipophilic phenolic compounds in the leaves of *E. actoni* and *E. virginensis* was indicated by blue fluorescing spots (visible under $UV_{366\,nm}$) after TLC of the dichloromethane extract. The main component was isolated by combined CC on silica gel and on Sephadex LH-20, and could be shown to be a mixture of the angelic (**1**) and the senecic acid esters (**2**) of 2-acetoxy-5-(1ξ-hydroxyethyl)-6-methoxy-benzofuran (ratio—from NMR—*ca* 6:1). The ^{1}H NMR spectrum of **1** (Table 1) shows the protons at C-4 and C-7 of the benzene ring as broadened singlets characteristic for the substitution pattern. The furan C-3 proton has suffered a large

Table 1. ^{1}H NMR data of **1** and **2** [multiplicity, δ (ppm), J (Hz), coupling group; integration confirms the number of H present in the various functionalities listed below]

	1			**2**	
H-3	7.42 *d**	0.9 (H-7)		7.41 *d*	0.9 (H-7)
H-4	7.61 *s* (*br*)			7.61 *s* (*br*)	
H-7	7.01 *s* (*br*)			7.00 *s* (*br*)	
MeO	3.90 *s*			3.89 *s*	
Ac	2.54 *s*			2.54 *s*	
MeCH(OCOR)	6.30 *q*	6.5 (Me)		6.24 *q*	6.5 (Me)
MeCH(OCOR)	1.52 *d*†	6.5 (CH)		1.49 *d*	6.5 (CH)
angelic acid			senecic acid:		
CO–C(=)–Me	1.94 *dq*‡	1.5 (Me)	=C–Me (*trans*)	1.89 *d*	1.3 (CH)
		1.4 (CH)			
=CH–Me	6.06 *qq*	7.2 (Me)	=C–Me (*cis*)	2.14 *d*	1.1 (CH)
		1.4 (Me)	CO–CH=	5.75 *m*	
=CH–Me	1.98 *dq*‡	1.5 (Me)			
		7.2 (CH)			

*s upon irradiation at 7.0 ppm.
†s upon irradiation at 6.3 ppm.
‡q upon irradiation at 6.1 ppm.



downfield shift as compared with 2-isopropylidene benzofurans [2] which is typical of 2-acetyl benzofurans (cf., e.g. 2,5-diacetylbenzofuran [10], δ (CH-3) 7.50). For the substituents (Ac, OMe and Me·CHOCOR·Ar) see Table 1. The presence of the angelic acid residue is evidenced by two double quartets (Me groups) and a quartet of quartets (olefinic H) (cf. [7]). For **2** the ^{1}H NMR signals of the alcohol moiety duplicate those of **1** except for a slight upfield shift (see Table 1). The senecic acid residue can be recognized by the two Me doublets and a multiplet for the olefinic proton [7]. The mass spectrum of the mixture shows $[M]^+$ at m/z 316. Exact mass measurement gives an elemental composition of $C_{18}H_{20}O_5$. The main fragment arises from the loss of $^{\cdot}OCOC_4H_7$ (m/z 217) accompanied by $[M - {}^{\cdot}COC_4H_7]^+$ (m/z 233) typical of *o*-OMe benzyl alcohol ester type structures [11]. In the lower mass range m/z 83 $[C_4H_7CO]^+$, 55 $[C_4H_7]^+$ and 43 $[Ac]^+$ can be recognized. 2-Acetylbenzofurans are found very rarely in the Asteraceae [12] and are known so far only from *Isocoma wrightii* [10]. *E. californica* [13] and *Enceliopsis nudicaulis* [7]. The cooccurence of these unusual compounds in the latter two species and also in *E. actoni* and *E. virginensis* seems interesting for systematic reasons since *Encelia* and *Enceliopsis* are considered to be closely related from morphological arguments [9]. Further research on the occurrence of 2-acetylbenzofurans in *Encelia* and related genera is in progress.

EXPERIMENTAL

MS were recorded at 70 eV, direct inlet and ^{1}H NMR at 300 MHz ($CDCl_3$, TMS, δ values).

Angelic and senecic esters of 2-acetoxy-5-(1ξ-hydroxyethyl)-6-methoxybenzofuran. E. actoni and *E. virginensis* were collected in the Mojave desert in spring 1982. The plant species have been identified by Dr. C. Clark, California State University, Pomona. Specimens have been deposited at the herbarium there. Air dried leaves were ground and extracted with $CHCl_3$. The extract was separated by CC on silica gel using $CHCl_3$ as eluent followed by repeated CC on Sephadex LH-20 using MeOH as eluent. Fractions containing 20 ml were monitored by TLC on silica gel, solvent CH_2Cl_2, detection under $UV_{366\,nm}$. Compounds **1** and **2** appeared together as one blue fluorescing spot under UV. ^{1}H NMR: see Table 1 and text. MS m/z (rel. int.): 316.1331 (36) (calc. for $C_{18}H_{20}O_5$ 316.1311): $[M]^+$ 233.0809 (14) (calc. for $C_{13}H_{13}O_4$ 233.0813). $[M - {}^{\cdot}COC_4H_7]^+$, 217.0871 (100) (calc. for $C_{13}H_{13}O_3$ 217.0865) $[M - {}^{\cdot}OCOC_4H_7]^+$, 216 (15) $[M - HOCOC_4H_7]^{+\cdot}$, 202 (18) $[217 - {}^{\cdot}Me]^{+\cdot}$, 201 (22) [$m/z$ 216 $- {}^{\cdot}Me]^+$, 187 (14), 83.0513 (46) (calc. for C_5H_7O 83.0496): $[C_4H_7CO]^+$, 55 (25) $[C_4H_7]^+$, 43 (88) $[Ac]^+$.

Acknowledgement—This project was supported by a grant of the Deutsche Forschungsgemeinschaft awarded to P.P.

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Phytochemistry, Vol. 24, No. 12, pp. 3071–3072, 1985.
Printed in Great Britain.

0031–9422/85 $3.00 + 0.00

BENZYL BENZOATES AND *o*-HYDROXYBENZYL FLAVANONES FROM *UVARIA FERRUGINEA*

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(*Received* 7 *March* 1985)

Key Word Index—*Uvaria ferruginea*; Annonaceae; benzyl benzoates; chamanetin; chamanetin 5-methyl ether; *o*-hydroxybenzyl flavanones; biogenesis.

Abstract—The isolation of benzyl benzoates and *o*-hydroxybenzyl flavanones from *Uvaria ferruginea*, in addition to the previously reported cyclohexene oxides, provides evidence in support of the proposed biogenetic route to these compounds via the common benzyl benzoate precursor.

Cyclohexene oxides form a small class of plant metabolites and interest in these unusual compounds has raised the question of their biogenesis. Two hypothetical pathways have been proposed, the first by Ganem and Hobbert [1] and the second by Jolad *et al.* [2]. The latter pathway postulated benzyl benzoate as the common origin of both the cyclohexene oxides and the *o*-hydroxybenzyl group in *o*-hydroxybenzyl dihydrochalcones and flavanones. In this paper we report the isolation of two benzyl benzoates and two *o*-hydroxybenzyl flavanones from *Uvaria ferruginea*. This co-isolation, in addition to the previously reported cyclohexene oxides from the same plant [3], is, to the best of our knowledge, the first observation of the co-occurrence of these three types of compounds. As can be readily seen, the implication of this observation is significant and would seem to put the Jolad *et al.* biogenetic hypothesis on firm ground.

Hexane extraction of the root of *U. ferruginea* followed by purification by CC yielded, apart from (−)-1,6-desoxysenepoxide (**1**), (−)-1,6-desoxytingtanoxide (**2**), α-senepoxide (**3**), tingtanoxide (**4**) and β-senepoxide (**5**) as previously reported [3], also benzyl benzoate (**6**) and 2-methoxybenzyl benzoate (**7**) in 0.011 and 0.016% yields, respectively. Further extraction of the plant material with chloroform gave chamanetin 5-methyl ether (**8**) [4] (0.01%). Similarly the stem of *U. ferruginea* afforded **4**–**7** from a hexane extract, while a chloroform extract yielded chamanetin (**9**) [5] (0.00057%).

The flavanone **9** and its monomethylated product **8** were identified by their spectroscopic data and by direct comparison with the natural products obtained by Professor Hufford. The structures of the compounds were also confirmed by chemical correlations. Thus treatment of either **8** or **9** with dimethylsulphate and K_2CO_3 in acetone gave the same fully methylated product **10**.

EXPERIMENTAL

^{1}H NMR: 60 MHz, TMS as int. standard; EIMS: probe 70 eV.

Extraction and separation. Ground, air-dried roots of *U. ferruginea* (3 kg), collected from Khonkhaen University campus, Khonkhaen Province, Northeast Thailand, were extracted with hexane (8 l.) at room temp. for 7 days, after which the extract was

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