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# THE BENZOFURAN NORWEDELIC ACID FROM *WEDELIA CALENDULACEAE*

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**Key Word Index**—*Wedelia calendulaceae*; Compositae; leaves; norwedelolactone; norwedelic acid; benzofuran.

**Abstract**—A new compound norwedelic acid [5,6-dihydroxy-2(2′,4′,6′-trihydroxyphenyl)-benzofuran-3-carboxylic acid] has been isolated from fresh leaves of *Wedelia calendulaceae* apart from norwedelolactone, a compound previously found in *Eclipta alba.*

## INTRODUCTION

The isolation of wedelolactone, the first naturally occurring coumaranocoumarin from the leaves of *Wedelia calendulaceae* Less., an Indian medicinal plant, was reported many years ago [1]. During a reinvestigation of this plant, besides wedelolactone (**1**) and norwedelolactone (**2**, isolated earlier from *Eclipta alba* Hassk. [2]) was obtained the hitherto unknown norwedelic acid (**3**). The structure of norwedelic acid was apparent from the spectral data (Table 1 and Experimental) and its conversion to *O*-methylwedelolactone by ethereal diazomethane.

The UV spectrum of norwedelic acid (**3**) is similar to that of wedelolactone (**1**) and norwedelolactone (**2**) indicating the presence of the same chromophore. In the IR spectrum the presence of a band at 1685 $cm^{-1}$ rather than 1710 $cm^{-1}$ indicates the presence of a free carboxyl group. The $^1H$ NMR spectrum shows that the two one-proton doublets at $\delta$6.48 and 6.62 in the spectrum of wedelolactone is replaced by a single two-proton signal in norwedelic acid (**3**) at $\delta$6.36 indicating the relatively free rotation of the phenyl group at position 2 of the benzofuran system. The above data leads to structure **3** for norwedelic acid.

There appears to be variation in the amounts of norwedelolactone and norwedelic acid isolated, depending on initial work up conditions leading to the suspicion that norwedelolactone could be an artefact arising during extraction.

## EXPERIMENTAL

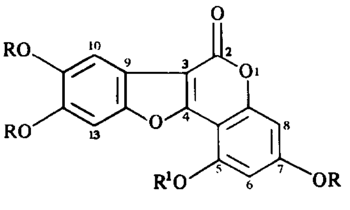
Mps are uncorr. IR spectra were recorded as KBr pellets except that of compound **4** run in $CHCl_3$, and UV spectra in 95% EtOH. NMR spectra were run at 90 MHz in DMSO-$d_6$ except that of **4** run in $CDCl_3$, all with TMS as internal reference.

Fresh leaves of *Wedelia calendulaceae* were freeze-dried and extracted with MeOH or ground as such in a blender with MeOH. The MeOH was then removed under red. pres. (bath temp 40–50°) to leave a residue. Water was added to the residue and the aq. layer extracted with $Et_2O$ to remove chlorophyll and other fatty substances. The aqueous layer was then filtered and extracted with *n*-BuOH. Removal of the solvent gave a residue chromatographed on Sephadex LH-20 using MeOH as eluant. TLC on silica gel plates using EtOAc–EtOH–$H_2O$ (8:2:1) was used to monitor the chromatography. Evaporation gave solids which were filtered off and crystallized from MeOH, where necessary rechromatography on Sephadex LH-20 using MeOH was carried out to give:

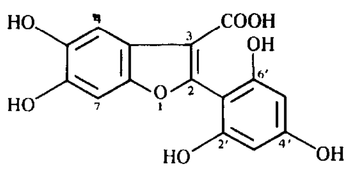
*Wedelolactone* (**1**). Mp 327–330° (d) (MeOH); $^1H$ NMR: $\delta$3.81 (*s*, 3H, OMe), 6.48, 6.62 (each *d*, each 1H, $J = 2.5$ Hz, H-6 or H-8) 7.18, 7.28 (*s*, each 1 H, H-10 or H-13), 9.1–9.83 (*br s*, 2H, phenolic OH).

*Norwedelolactone* (**2**). Mp > 360° (MeOH); $^1H$ NMR: $\delta$6.75, 6.92 (each *d*, each 1H, $J = 2.5$ Hz, H-6 or H-8), 7.20, 7.30 (each *s*, each 1H, H-10 and/or H-13), 9–9.68 (2H, *br s*, phenolic OH).

*Norwedelic acid* (**3**). Mp > 305° (d); MS *m/z*: 330 $[M - H_2O]^+$; $^1H$ NMR: $\delta$6.36 (*s* with fine splitting, 2H, H-4 or H-7), 7.13, 7.2 (eash *s*, each H, either H-3′ or H-5′), 9.06–9.6 (*br s*, 2H,



**1** $R^1 = Me$, $R = H$
**2** $R^1 = R = H$
**4** $R^1 = R = Me$



**3**

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

| Compound | UV $\lambda_{max}$ (nm) | IR $\nu_{max}$ (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: $\delta$3.80, 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).

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# BENZOFURAN DERIVATIVES FROM TWO *ENCELIA* SPECIES

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**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