$[C_9H_6O_2]^+$ (37.1), 137 (17.5), 136 $[C_7H_4O_3]^+$ (41.2), 69 $[C_5H_9]^+$ (58.2).

*Maxima isoflavone H*. Colourless prisms, mp 190–191.5°, showed green colour in Labat test, analysed for $C_{17}H_{12}O_5$, UV $\lambda_{max}^{MeOH}$ nm: 210, 259, 298; IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3050, 1622, 1580, 1030, 940, 772; $^1$H NMR (90 MHz, $CDCl_3$): $\delta$7.88 (1H, *s*, H-2), 7.87 (1H, *d*, $J = 9$ Hz, H-5), 6.94 (1H, *d*, $J = 9$ Hz, H-6), 7.46 (2H, *d*, $J = 9$ Hz, H-3′, H-5′), 6.94 (2H, *d*, $J = 9$ Hz, H-2′, H-6′), 6.18 (2H, *s*, $-OCH_2O-$), 3.83 (3H, *s*, $OCH_3$-4′); MS *m/z* (rel. int.): 297 (19.4), 296 $[M]^+$ (100), 295 (20.7), 281 $[M-CH_3]^+$ (11.9), 165 $[C_8H_5O_4]^+$ (8), 164 $[C_8H_4O_4]^+$ (83.1), 132 $[C_9H_8O]^+$ (27.2), 117 $[C_8H_5O]^+$ (8.1).

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# A BENZOFURAN FROM *TAGETES PATULA* SEEDLINGS

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**Key Word Index**—*Tagetes patula*; Compositae; seedlings; benzofurans; 4-hydroxydehydrotremetone (isoeuparin).

**Abstract**—Two benzofurans, 4-hydroxydehydrotremetone and hydroxytremetone, have been isolated from roots and hypocotyls of seedlings. 4-Hydroxydehydrotremetone represents a hitherto undescribed compound.

## INTRODUCTION

Benzofurans are characteristic natural products of certain tribes of the Asteraceae [1]. In continuation of our phytochemical investigations of *Tagetes* we report here the isolation and structural elucidation of a new benzofuran, 4-hydroxydehydrotremetone (isoeuparin), in seedlings of *Tagetes patula* L. as well as hydroxytremetone.

## RESULTS AND DISCUSSION

Compound **1**, isoeuparin, $C_{13}H_{12}O_3$, $[M]^+$ 216.0793 (high resolution MS), exhibited typical IR absorption bands of a hydrogen-bonded carbonyl group (1622 cm$^{-1}$), aromatic ring (1575 cm$^{-1}$) and a hydroxyl group (2926 cm$^{-1}$). The 400 MHz $^1$H NMR spectrum ($CDCl_3$) showed that compound **1** is very similar to euparin **2**, with a phenolic hydroxyl proton at $\delta$13.23 characteristic of an *o*-hydroxyketone, two broadened one-proton singlets at $\delta$5.20 and 5.78 corresponding to a methylene group, and three-proton signals for the vinylic methyl group ($\delta$2.12, broad singlet) and for the sharp singlet at $\delta$2.67, which strongly suggest that the ketone is in fact a methyl ketone. This conclusion is partially supported by the presence of the base peak at $[M-15]^+$ (*m/z* 201) in its mass spectrum.

The assignment of the aromatic protons at C-6 and C-7 revealed the only difference between the $^1$H NMR spectrum of **1** and **2**. They appeared as a one-proton doublet at $\delta$7.64 ($J = 8.7$ Hz) and a doublet of doublets at $\delta$7.00 ($J = 8.7$, 1.0 Hz), respectively. As shown by double resonance experiments, the one-proton broad singlet at $\delta$6.84

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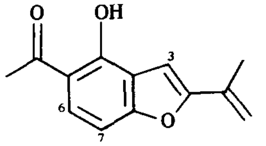

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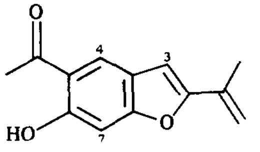

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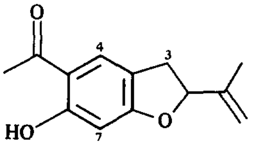

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corresponding to H-3 (the only remaining signal) was found to be long-range coupled to the aromatic proton at C-7 ($J = 1.0$ Hz). Long-range proton–proton couplings of similar magnitude between the approximately *trans*-disposed H-3 and H-7, in benzofuran and indene have been observed [3].

GC/MS analysis has led us to the conclusion that hydroxytremetone (3) is also present in seedlings. This compound has previously been found in *Tagetes* spp. [4] and also in *Liatris provincialis* [5].

## EXPERIMENTAL

*Plant material.* Seedlings of *T. patula* cv. "Zitronenzwerg" were grown in moist vermiculite under conditions of illumination described previously [6].

*Isolation and purification of* **2** *and* **3**. *Tagetes* roots and hypocotyls were homogenized in EtOH and extracted with petrol [6]. After evaporation to dryness, the residue was dissolved in EtOH. 100 μl of this soln was immediately subjected to semi-preparative HPLC (col. 8 × 250 mm; Lichrosorb RP 18, 5 μ, Merck, Darmstadt, F.R.G.; gradient: linear 75% MeCN–25% $H_2O$ to 100% MeCN (15 min), then 100% MeCN for 15 min, flow 2.5 ml/min. Detection spectrophotometrically at 333 nm). Fractions containing the benzofurans **2** and **3** were collected and freeze-dried.

*Compound* **1**. This product was purified by prep. TLC on Merck silica gel 60 $F_{254}$ using $Et_2O$–petrol (1:1) as solvent system. It was located ($R_f$ 0.80) by shortwave UV light and recrystallized as yellowish needles from *n*-hexane mp 107–108°. It gave a green colour reaction with $FeCl_3$. UV $\lambda_{max}^{MeOH}$ nm: 338, 298 (sh), 270, 242 (sh); MS *m/z* (rel. int.): 216.0793 $[M]^+$ (89), 201 $[M - Me]^+$ (100), 198 $[M - H_2O]^+$ (14), 183 $[M - Me - H_2O]^+$ (3), 173 $[M - MeCO]^+$ (8), 115 $[C_9H_7]^+$ (19), 43 $[MeCO]^+$ (39).

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