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EUPATARONE, A 2-ACETYLBENZOFURAN FROM *EUPATORIUM STERNBERGIANUM*

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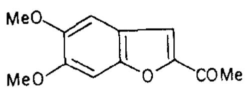
Key Word Index—*Eupatorium sternbergianum*; Compositae; aerial parts; benzofuran; triterpenes; flavanones; eupatarone.

Abstract—A new benzofuran, eupatarone, together with 2-hydroxy-4, 5-dimethoxybenzaldehyde, 12-hydroxy-2, 3-dihydroeuparine, spathulenol, precocene II, dammaradienol, dammaradienol acetate, 5, 3′-dihydroxy-7, 4′-dimethoxyflavanone and 5, 7-dihydroxy-4′-methoxyflavanone, have been isolated from aerial parts of *Eupatorium sternbergianum*.

In continuation of our work on the constituents of the genus *Eupatorium* [1–3], the present communication describes the isolation and structural determination of a new benzofuran, eupatarone, and other constituents of *Eupatorium sternbergianum*.

Eupatarone is a solid of empirical formula $C_{12}H_{12}O_4$. Its IR spectrum shows the presence in the molecule of an aromatic ring and a carbonyl group. In the NMR there are signals typical of an acetyl and two methoxyl groups; signals of three uncoupled protons also appear in the aromatic region. The mass spectrum shows the molecular ion at m/z 220. The loss of a methyl or an acetyl group gives two ions at m/z 205 and 177 respectively. This spectroscopic information suggests that eupatarone has structure **1**. This was proved by hydrogenation, when **2** and **3** were obtained and identified on the basis of their spectral data. Moreover, eupatarone was identical with a synthetic sample [4, 5]. Therefore it must be 2-acetyl-5, 6-dimethoxybenzofuran. It may be derived from an isopropylbenzofuran precursor by oxidative removal of the exocyclic double bond [6]. The only two compounds of this type isolated previously are euparone methyl ester from *Encelia californica* [6] and 2, 5-diacetylbenzofuran from *Haplopappus heterophyllus* [7].

From *Eupatorium sternbergianum* we have also isolated 2-hydroxy-4, 5-dimethoxybenzaldehyde, 5, 3′-dihydroxy-7, 4′-dimethoxyflavanone (persicogenin) [8] and 5, 7-dihydroxy-4′-methoxyflavanone (isosakuranetin) [9], the sesquiterpene spathulenol [10], the triterpenes dammaradienol and dammaradienol acetate, the benzofuran 12-hydroxy-2, 3-dihydroeuparine [11], the sterols sitosterol, campesterol and stigmasterol, and the anti-juvenile hormone, precocene II (ageratochromene) [12, 13]. This last compound is the most abundant constituent in this species.



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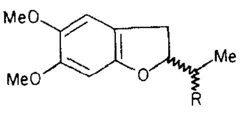

2 R = OH
3 R = H

EXPERIMENTAL

Mps are uncorr. ^{1}H NMR spectra were run on a 90-MHz and ^{13}C NMR on a 20-MHz instrument in $CDCl_3$ with TMS as int. ref. Column and dry column chromatography were performed on Si gel.

Isolation of the products. The air-dried aerial parts of *Eupatorium sternbergianum* DC (2.5 kg) collected at Huarochiri, Lima, Peru, were finely cut and extracted with EtOH. Combined filtered ethanolic extracts were concd *in vacuo* and chromatographed. A petrol–EtOAc mixture eluted a variety of products, which were rechromatographed on dry column, yielding the following compounds in order of elution: dammaradienol acetate (700 mg), spathulenol (110 mg), precocene II (3.7 g), dammaradienol (950 mg), 2-hydroxy-4, 5-dimethoxybenzaldehyde (90 mg), 5, 3′-dihydroxy-7, 4′-dimethoxyflavanone (30 mg), 5, 7-dihydroxy-4′-methoxyflavanone (20 mg), eupatarone (230 mg) and 12-hydroxy-2, 3-dihydroeuparine (65 mg).

Known compounds were identified by spectral data. We give here the previously unreported ^{13}C NMR spectra of dammaradienol and its acetate. Dammaradionol acetate: 38.9 (C-1), 23.7 (C-2), 80.3 (C-3), 37.9 (C-4), 56.0 (C-5), 18.2 (C-6), 34.3 (C-7), 40.5 (C-8), 50.9 (C-9), 37.2 (C-10), 21.4 (C-11), 29.0 (C-12), 45.4 (C-13), 49.4 (C-14), 27.1 (C-15), 35.4 (C-16), 45.4 (C-17), 16.3 (C-18), 15.7 (C-19), 152.5 (C-20), 107.6 (C-21), 31.4 (C-22), 25.0 (C-23), 124.5 (C-24), 131.3 (C-25), 17.7 (C-26), 25.7 (C-27), 28.0 (C-28), 16.5 (C-29), 15.9 (C-30). Dammaradienol: 39.2 (C-1), 27.4 (C-2), 78.9 (C-3), 39.0 (C-4), 55.9 (C-5), 18.3 (C-6), 34.2 (C-7), 40.5 (C-8), 51.0 (C-9), 37.2 (C-10), 21.4 (C-11), 28.9 (C-12), 45.3 (C-13), 49.5 (C-14), 27.1 (C-15), 35.5 (C-16), 47.8 (C-17), 15.7 (C-18), 16.2 (C-19), 152.6 (C-20), 107.5 (C-21), 31.4 (C-22), 25.0 (C-23), 124.5 (C-24), 131.3 (C-25), 17.7 (C-26), 25.7 (C-27), 28.1 (C-28), 15.4 (C-29), 16.0 (C-30).

Eupatarone (**1**). Mp 116–117° (lit. 115.5–117.5, [5]). IR $\nu_{max}^{CHCl_3}$ cm^{-1} 3010, 3000, 1675, 1618, 1550, 1485, 1315, 1295, 1145, 1005, 845. UV (EtOH) λ_{max} nm: 223, 262, 301 and 336. ^{1}H NMR 2.52 (3H, *s*), 3.91 and 3.96 (each 3H, *s*), 7.05 (2H, *s*), 7.62 (1H, *s*). MS *m/z* 220.0720 (M$^+$, $C_{12}H_{12}O_4$), 205.0448 (M$^+$ – CH$_3$), 177.0560 (M$^+$ – C_2H_3O), 149.0590 (M$^+$ – $C_3H_3O_2$), 135.0428 (M$^+$ – $C_4H_5O_2$). Found: C, 65.27; H, 5.48. Calc. $C_{12}H_{12}O_4$ requires: C, 65.45; H, 5.49.

Hydrogenation of eupatarone. **1** (70 mg) was dissolved in EtOH (20 ml) and hydrogenated for 3 hr over Pd–C (10%). This gave after chromatography (Si gel, Be) two components: **3** (20 mg) ^{1}H NMR 9.00 (3H, *t*), 1.70 (2H, *m*), 2.70 and 3.13 (each 1H, *q*, $J = 14, 8$ Hz), 3.68 and 3.74 (each 3H, *s*), 4.56 (1H, *q*), 6.26 and 6.60 (each 1H, *s*). MS *m/z* 208 (M$^+$), 193, 82. **2** (22 mg) ^{1}H NMR 1.16 (3H, *dd*), 3.00 (2H, *m*), 6.68 and 6.72 (each 3H, *s*), 3.90 (1H, *m*), 4.51 (1H, *m*), 6.27 (1H, *d*), 6.62 (1H, *brs*). MS *m/z* 224 (M$^+$), 209, 191, 179, 167, 83.

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AMORININ, A PRENYLATED CHROMENOFLAVANONE FROM *AMORPHA FRUTICOSA*

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Key Word Index—*Amorpha fruticosa*; Leguminosae; amorinin; prenylated flavanone.

Abstract—A diprenylated chromenoflavanone has been characterized from the root bark of *Amorpha fruticosa*.

From the roots of *Amorpha fruticosa* L. amorphigenin, formononetin, ononin, wistin and amorphaquinone have been isolated recently by Shibata *et al.*[1]. In the course of our investigation on the constituents of the root-bark of the plant, a new prenylated chromenoflavanone (**1**) has been obtained, named amorinin. The present communication reports the structural determination of this oily component.

The presence of phenolic hydroxyl groups in **1** was indicated by the strong coloration with methanolic ferric chloride. The compound has UV absorption characteristic for flavanone derivatives[2] (λ_{max}^{MeOH} nm) log ϵ [273 sh (4.27), 285 (4.35), 300 (4.39) and 345 (4.07)].

The ^{1}H NMR spectrum (90 MHz, CDCl$_3$) shows two isopentenyl side-chains (δ 5.31, *m*, 3H, 2*x* –CH$_2$–$\underline{\mathrm{CH}}$= + H-2; 3.31, *m*, 4H, 2*x* –$\underline{\mathrm{CH}_2}$–CH=; 1.73, *s*, 6H, 2*x* –CH$_3$; 1.71, *s*, 6H, 2*x* –CH$_3$) and one 2,2-dimethylchromene moiety (δ 6.32, *d*, 1H, $J = 9.9$ Hz, H-4″; 5.64, *d*, 1H, $J = 9.7$ Hz, H-3″). The singlet at δ