EUPATARONE, A 2-ACETYLBENZOFURAN FROM *EUPATORIUM STERNBERGIANUM*

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(Received 6 October 1981)

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-dihydro-

euparine [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.

EXPERIMENTAL

Mps are uncorr. 1H 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. Dammaradienol 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,

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2 R = OH
3 R = H

1145, 1005, 845. UV (EtOH) $\lambda_{\max}$ nm: 223, 262, 301 and 336. ^1H 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^+ , $\text{C}_{12}\text{H}_{12}\text{O}_4$), 205.0448 ($\text{M}^+ - \text{CH}_3$), 177.0560 ($\text{M}^+ - \text{C}_2\text{H}_3\text{O}$), 149.0590 ($\text{M}^+ - \text{C}_3\text{H}_5\text{O}_2$), 135.0428 ($\text{M}^+ - \text{C}_4\text{H}_7\text{O}_3$). Found: C, 65.27; H, 5.48. Calc. $\text{C}_{12}\text{H}_{12}\text{O}_4$ 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) ^1H 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) ^1H 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.

Acknowledgements—We wish to thank the Instituto de Cooperación Iberoamericana (Madrid), for financial support and Dr Ramón Ferreyra (Museo de Historia Natural, Universidad Mayor de San Marcos, Lima) for collecting and classifying the plant material. V.P.G. thanks the Island Council of La Palma for a grant.

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Phytochemistry, Vol. 21, No. 7, pp. 1827–1828, 1982.
Printed in Great Britain.

0031-9422/82/071827-02\$03.00/0
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AMORININ, A PRENYLATED CHROMENOFILAVANONE FROM *AMORPHA FRUTICOSA*

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(Received 16 October 1981)

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. amorphenin, 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] ($\lambda_{\max}^{\text{MeOH}}$ nm) $\log \epsilon$ [273 sh (4.27), 285 (4.35), 300 (4.39) and 345 (4.07)].

The ^1H NMR spectrum (90 MHz, CDCl_3) shows two isopentenyl side-chains (δ 5.31, m, 3H, 2x $-\text{CH}_2-\text{CH}=\text{CH}-\text{H}$; 3.31, m, 4H, 2x $-\text{CH}_2-\text{CH}=\text{CH}-\text{H}$; 1.73, s, 6H, 2x $-\text{CH}_3$; 1.71, s, 6H, 2x $-\text{CH}_3$) 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