

inseparable from and identical with  $\alpha$ -spinasteryl acetate,  $R_f$  0.58. Examination of the benzoate derivative, however, revealed that the material is actually composed of three sterols having  $R_f$  0.34 (I), 0.53 (II), 0.65 (III).

The MS<sup>4,5</sup> of the isolated sterol mixture indicated that sterol I is a C<sub>29</sub>H<sub>48</sub>O sterol (M<sup>+</sup>,  $m/e$  412), containing two double bonds, which exhibited the fragmentation pattern expectable for  $\alpha$ -spinasterol. The principal features of this pattern include the loss of a monounsaturated C<sub>10</sub>H<sub>19</sub> side chain alone and together with 42 m.u., and the expulsion of butadiene from ring A in dehydroxylated ion species. Sterol II is stigmastenol, C<sub>29</sub>H<sub>50</sub>O (M<sup>+</sup>,  $m/e$  414) containing one double bond located in the steroid nucleus. This was evidenced by the total loss of the saturated side chain C<sub>10</sub>H<sub>21</sub>. Sterol III is stigmastanol, C<sub>29</sub>H<sub>52</sub>O (M<sup>+</sup>,  $m/e$  416) which is fully saturated. The observed fragmentations are those expectable for saturated sterols and include products resulting from break down of ring A in the dehydroxylated ion species by a retro-Diels-Alder type of reaction.

The unsaponifiable fraction of the seed fat afforded a sterol mixture which was found to be identical with that isolated from the leaves.

<sup>4</sup> BUDZIKIEWICZ, H., DJERASSI, C. and WILLIAM, D. H. (1964) *Structure Elucidation of Natural Products by Mass Spectrometry*, Vol. 2, p. 21, Holden-Day, New York.

<sup>5</sup> WULFSON, N. S., ZARETSKII, V. I. and TORGOF, I. V. (1964) *Tetrahedron Letters* 3015.

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### 5,4'-DIHYDROXY-3,7-DIMETHOXYFLAVONE FROM *AMBROSIA ERIOCENTRA*

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**Key Word Index**—*Ambrosia eriocentra*; Compositae; flavonol; kaempferol 3,7-dimethyl ether.

*Plant.* *Ambrosia eriocentra* (Gray) Payne. *Source.* Collected by R. J. Barr on 3 May 1965, and on 3 May 1967, near Wickenburg, Maricopa County, Arizona. (Barr No. 65-191 and 67-143 on deposit in herbarium of Florida State University.) *Previous work.* No crystalline sesquiterpene lactones.<sup>1</sup>

*Isolation and identification.* The above-ground parts of Barr No. 65-143, wt 9.8 kg, were extracted with CHCl<sub>3</sub> and worked up in the usual fashion.<sup>2</sup> The crude gum, wt 31.9 g, was only sparingly soluble in benzene or CHCl<sub>3</sub>. It was dissolved in 1:1 C<sub>6</sub>H<sub>6</sub>-CHCl<sub>3</sub> with the aid of some EtOH and chromatographed over 500 g of silicic acid in the usual manner. 24 g of gum was recovered from the first 4 l. of eluate; subsequent fractions consisted of gummy mixtures. The gum from the first 4 l. of eluate was redissolved in

<sup>1</sup> HIGO, A., HAMMAM, Z., TIMMERMAN, B. N., YOSHIOKA, H., LEE, J., MABRY, T. J. and PAYNE, W. W. (1971) *Phytochemistry* 10, 2241.

<sup>2</sup> HERZ, W. and HÖGENAUER, G. (1962) *J. Org. Chem.* 27, 905.

$C_6H_6-CHCl_3$  (1:1) with the aid of a few ml of EtOH. Addition of 100 g of silica gel followed by evaporation of solvent gave a free-flowing powder which was placed on a column of 500 g of silicic acid and rechromatographed in the usual manner, 1 l. fractions being collected. The only solid material was found in fractions 91–93 ( $CHCl_3$ –MeOH 99:1). Recrystallization afforded 0.25 g of 5,4'-dihydroxy-3,7-dimethoxyflavone, m.p. 246–248° (lit 253–254°, 246–247°), NMR signals (DMSO- $d_6$ ) at 7.91  $\delta$  and 6.90  $\delta$  (J 9,  $A_2B_2$  system of H-2', H-3', H-5' and H-6'), 6.62  $\delta$  and 6.27  $\delta$  (J 2, AB system of H-6 and H-8), 3.82 and 3.78 (two methoxyls), UV  $\lambda_{max}$  352.5 and 267 nm, with added NaOAc 355 and 268 nm, with added  $AlCl_3$  352.5, 305 and 277 nm, with added NaOEt 395 and 270 nm, with added NaOAc– $H_3BO_3$  350 and 267 nm. Direct comparison with an authentic sample of 5,4'-dihydroxy-3,7-dimethoxyflavone supplied by Prof. P. R. Jefferies established identity. Extraction of Barr No. 65-191 gave similar results.

The present report corroborates the findings of Higo *et al.*<sup>1</sup> that *A. eriocentra* yields no easily crystallizable homogeneous sesquiterpene lactone components. 5,4'-Dihydroxy-3,7-dimethoxyflavone has previously been isolated from an unnamed new *Beyeria* species,<sup>3</sup> from *Alpinia Kumatake*,<sup>4</sup> *A. japonica*,<sup>5</sup> *Eucryphia lucida*,<sup>6</sup> *Cistus ladanifera*,<sup>7</sup> *Cheilanthes farinosa*<sup>8</sup> and *Larrea cuneifolia*,<sup>9</sup> but not, to the best of our knowledge, from a Composite.

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<sup>3</sup> JEFFERIES, P. R. and PAYNE, T. G. (1965) *Australian J. Chem.* **18**, 1441.

<sup>4</sup> KIMURA, Y., TAKIDA, M., TAKAHASHI, S. and KIMISHIMA, M. (1967) *Yakugaku Zasshi* **87**, 440.

<sup>5</sup> KIMURA, Y., TAKIDA, M. and TAKAHASHI, S. (1967) *Yakugaku Zasshi* **87**, 1132.

<sup>6</sup> BATE-SMITH, E. C., DAVENPORT, S. M. and HARBORNE, J. B. (1967) *Phytochemistry* **6**, 1407.

<sup>7</sup> DE PASCUAL TERESA, J., PORTELA MARCOS, C. and SANCHEZ BEILIDO, I. (1960) *An. Quim.* **64**, 623.

<sup>8</sup> RANGASWAMI, S. and IYER, R. T. (1969) *Indian J. Chem.* **7**, 526.

<sup>9</sup> VALESI, A. G., RODRIGUEZ, E., VANDERVELDE, G. and MABRY, T. J. (1972) *Phytochemistry* **11**, 2821.

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## 6-PHENYLETHYL-5,6-DIHYDRO-2-PYRONES FROM *ANIBA GIGANTIFOLIA*\*

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**Key Word Index**—*Aniba gigantifolia*; Lauraceae; anibine, substituted (6S)-phenylethyl-5,6-dihydro-2-pyrones.

Several *Aniba* species contain 4-methoxy-6-styryl-2-pyrones (I).<sup>2</sup> Metabolites of this type are accompanied in two *Piper* species by dihydro (II) and tetrahydro (III) deriva-

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<sup>2</sup> GOTTLIEB, O. R. (1972) *Phytochemistry* **11**, 1537.