5. Mabry, T. J., Markham, K. R. and Thomas, M. B. (eds) (1970) *The Systematic Identification of Flavonoids*. Springer, New York.
6. Rama Rao, A. V., Rathi, S. S. and Venkataraman, K. (1972) *Indian J. Chem.* **10**, 989.
7. Rahman, W. and Ilyas, M. (1962) *J. Org. Chem.* **27**, 153.
8. Harborne, J. B. (1965) *Phytochemistry* **4**, 107.
9. Fox, D. W., Savage, W. L. and Wender, S. H. (1953) *J. Am. Chem. Soc.* **75**, 2504.
10. Horowitz, R. M. and Gentili, B. (1966) *Chem. Ind.* (*London*) 625.
11. Thomas, M. B. and Mabry, T. J. (1968) *Phytochemistry* **7**, 787.

Phytochemistry, Vol. 24, No. 4, pp. 875–876, 1985.
Printed in Great Britain.

0031–9422/85 $3.00 + 0.00

FURTHER STUDIES ON THE ISOFLAVONES OF *TEPHROSIA MAXIMA*

E. Venkata Rao and M. Sree Rama Murthy

Department of Pharmaceutical Sciences, Andhra University, Waltair 530003, India

(*Received* 30 *July* 1984)

Key Word Index—*Tephrosia maxima*; Leguminosae; isoflavones; maxima isoflavone B; maxima isoflavone H.

Abstract—A new 7,8-methylenedioxyisoflavone, maxima isoflavone H, was isolated from *Tephrosia maxima* along with the known isoflavone, maxima isoflavone B.

In continuation of our studies on the isoflavones of *Tephrosia maxima* [1], we report here the isolation and characterization of another new isoflavone designated as maxima isoflavone H, in addition to the known isoflavone maxima isoflavone B [2].

An isoflavone fraction obtained by chromatography of the root chloroform extract was found to run close to maxima isoflavones A and B. Although it gave a single spot in TLC, chemical ionization mass spectrometry showed it to be a mixture of three compounds [MS m/z (CH_4) (rel. int.): 351 (21), 311 (60.6), 297 (100), 283 (30)]. On coupling, the chemical ionization mass spectrometry with electron impact mass spectrometry and ^1H NMR, it was inferred that the substance was a mixture of maxima isoflavones A and B and a new isoflavone having a methylenedioxy substituent.

The mixture was treated with 2 M alcoholic hydrochloric acid [1] and the pure isoflavones isolated by CC of the hydrolysate. Maxima isoflavone A was first eluted along with maxima isoflavone H (both unaffected) followed by pseudobaptigenin (formed from maxima isoflavone B). Maxima isoflavone H was separated from maxima isoflavone A by repeated fractional crystallization.

Maxima isoflavone H gave a positive Labat test and showed carbonyl absorption at 1624 cm^{-1} in its IR spectrum. Its ^1H NMR spectrum revealed the presence of one methylenedioxy and one methoxy group. The presence of the methylenedioxy group in ring A and the methoxy group in ring B was evident from the mass spectrum of the compound. As expected [3], its mass spectrum gave $[M]^+$ 296 (100), 164 (83.1) corresponding to the A ring fragment ion, and 132 (27.2) corresponding to the B ring fragment ion. The ^1H NMR spectrum of the compound showed the position of the methylenedioxy substituent as 7.8 by its two *ortho* coupled doublets at δ7.87 and 6.94 ($J = 9$ Hz), each integrating for one proton, which can be assigned to H-5 and H-6, respectively [4]. The presence of the methoxy group at the 4′-position was inferred by the two doublets at δ7.46 and 6.94 ($J = 9$ Hz) each integrating for two protons. Thus, the structure of maxima isoflavone H was established as 7,8-methylenedioxy-4′-methoxyisoflavone. Maxima isoflavone H represents the third example of 7,8-methylenedioxyisoflavones, the first two being maxima isoflavone A [5] and maxima isoflavone D [1].

Maxima isoflavone B, the structure of which was established earlier as 7-γ,γ-dimethylallyloxy-3′,4′-methylenedioxyisoflavone by chemical degradation [6] and synthesis [7], has now been characterized by spectral data.

EXPERIMENTAL

Refer to our earlier paper [1] for plant material employed and extraction details. CC of the root $CHCl_3$ extract (24 g) yielded maxima isoflavone B (127 mg, R_f 0.78 in 5% Me_2CO in benzene) and maxima isoflavone H (54 mg, R_f 0.75 in 5% Me_2CO in benzene), apart from the previously reported isoflavones.

Maxima isoflavone B. Colourless needles, mp 126–128° identical with lit. [6] value (126–128°); UV λ_{max}^{MeOH} nm: 218, 252, 298; IR ν_{max}^{KBr} cm^{-1}: 1635, 1490, 1440, 925, 820, 782; ^1H NMR (90 MHz, $CDCl_3$): δ7.73 (1H, *s*, H-2), 8.04 (1H, *d*, $J = 9$ Hz, H-5), 6.70 (1H, *dd*, $J = 9$, 2 Hz, H-6), 6.95 (1H, *d*, $J = 2$ Hz, H-8), 6.8–7.2 (3H, *m*, H-2′, H-5′, H-6′), 5.9 (2H, *s*, $-OCH_2O-$), 4.53 (2H, *d*, H-1″), 5.38 (1H, *t*, H-2″), 1.75, 1.80 (6H, two *s*, CH_3-4″, CH_3-5″); MS m/z (rel. int.): 350 $[M]^+$ (10.2), 282 $[M - C_5H_8]^+$ (100), 146

$[C_9H_6O_2]^+$ (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 $\lambda_{\max}^{\mathrm{MeOH}}$ nm: 210, 259, 298; IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3050, 1622, 1580, 1030, 940, 772; ^{1}H NMR (90 MHz, $CDCl_3$): δ7.88 (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).

Acknowledgements—We are grateful to Dr. R. S. Kapil, Assistant Director, Medicinal Chemistry Division, CDRI, Lucknow, India for providing the chemical ionization mass spectra. One of us (M.S.R.M.) thanks the CSIR, New Delhi for a Senior Research Fellowship.

REFERENCES

1. Venkata Rao, E., Sree Rama Murthy, M. and Ward, R. S. (1984) *Phytochemistry* **24**, 1493.
2. Rangaswami, S. and Rama Sastry, B. V. (1954) *Curr. Sci. (India)* **23**, 397.
3. Mabry, T. J. and Markham, K. R. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds), p. 97. Chapman & Hall, London.
4. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) in *The Systematic Identification of Flavonoids*, p. 165. Springer, New York.
5. Rangaswami, S. and Rama Sastry, B. V. (1956) *Proc. Indian Acad. Sci.* **44A**, 279.
6. Rangaswami, S. and Rama Sastry, B. V. (1963) *Proc. Indian Acad. Sci.* **57A**, 135.
7. Kukla, A. S. and Seshadri, T. R. (1962) *Tetrahedron* **18**, 1443.

Phytochemistry, Vol. 24, No. 4, pp. 876–877, 1985.
Printed in Great Britain.
0031-9422/85 \$3.00+0.00

A BENZOFURAN FROM *TAGETES PATULA* SEEDLINGS

RAINER SÜTFELD, FELIPE BALZA* and G. H. NEIL TOWERS*†

Botanisches Institut, Westfalische Wilhelms-Universitat Munster, D-4400 Munster, West Germany; *Department of Botany, University of British Columbia, Vancouver, BC, Canada, V6T 2B1

(*Received* 6 *September* 1984)

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 δ13.23 characteristic of an *o*-hydroxyketone, two broadened one-proton singlets at δ5.20 and 5.78 corresponding to a methylene group, and three-proton signals for the vinylic methyl group (δ2.12, broad singlet) and for the sharp singlet at δ2.67, 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 δ7.64 ($J = 8.7$ Hz) and a doublet of doublets at δ7.00 ($J = 8.7$, 1.0 Hz), respectively. As shown by double resonance experiments, the one-proton broad singlet at δ6.84

---

†To whom all correspondence should be addressed.