Phytochemistry, 1980, Vol. 19, pp. 988–989. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0501-0988 $02.00/0

BARBIGERONE, A NEW PYRANOISOFLAVONE FROM SEEDS OF *TEPHROSIA BARBIGERA*

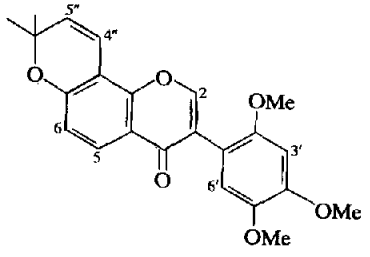
CHRISTIAN VILAIN

Natural Substances, Department of Organic Chemistry, University of Liège, Sart-Tilman by B-4000 Liege 1, Belgium

(*Received* 23 *July* 1979)

Key Word Index—*Tephrosia barbigera*; Leguminosae; barbigerone; 2′,4′,5′-trimethoxy-6″,6″-dimethylpyrano(2″,3″:7,8)isoflavone.

The genus *Tephrosia* is known to be rich in flavonoids, isoflavonoids and rotenoids of complex structures [1–6]. In the present study, a new isoflavone, barbigerone (**1**), was found as the major flavonoid of the seeds of *Tephrosia barbigera*, an annual species widespread in Zaïre.



1 Barbigerone

The compound analysed for $C_{23}H_{22}O_6$, M^+ 394,1417 ($C_{23}H_{22}O_6$ requires M^+ 394,1416). UV λ_{max}^{MeOH} nm(log ε): 236(4.35), 263(4.47), 294(4.08) and 323(sh 3.86) which remained unaffected on the addition of NaOAc or $AlCl_3$. NMR(100 MHz, $CDCl_3$; δ, TMS internal standard): a large singlet at 1.48 (6H, Me_2C<); three sharp singlets at 3.75, 3.84 and 3.91 (3H each, 2′,4′,5′-triMeO-); four one-proton doublets (which are typical of the indicated chromene ring system [7–11]) at 5.68 (H-5″, $J = 10$ Hz), 6.82 (H-4″, $J = 10$ Hz), 6.84 (H-6, $J = 9$ Hz) and 8.06 (H-5, $J = 9$ Hz); the two one-proton singlets at 6.62 (H-3′) and 6.97 (H-6′) indicate unequivocally a 2′,4′,5′-trioxygenation pattern for the side phenyl nucleus; finally, the sharp singlet at 7.96 (1H, H-2) which is a characteristic feature of isoflavones [13]. The MS showed prominent peaks at *m/e* (rel. int.) 394 (M^+, 100), 379 (88), 363 (42), 349 (26), 203 (14), 191 (19), 189,5 (31), 187 (19), 182 (19), 168 (26), 149 (11), which was consistent with the proposed structure.

Barbigerone is therefore a novel substance whose structure is closely related to that of the rotenoid, deguelin, which belongs to the restricted group of angular 5-deoxypyranoisoflavones. Only four other compounds of this type are known in nature; all from the Leguminosae: jamaïcin (2′-methoxy-4′,5′-methylenedioxy-6″,6″-dimethylpyrano(2″,3″:7,8)isoflavone) from *Piscidia erythrina* [7, 13], ferrugone (2′,5′-dimethoxy-3′,4′-methylenedioxy-6″,6″-dimethylpyrano(2″,3″:7,8)isoflavone) from *Milletia ferruginea* [8] and calopogoniumisoflavones A and B (respectively: 4′-methoxy- and 3′,4′-methylenedioxy-6″,6″-dimethylpyrano(2″,3″:7,8)isoflavone) from *Calopogonium muconoïdes* [9–11].

EXPERIMENTAL

Seeds of *Tephrosia barbigera* L. were collected from Kinshasa's Plateaus, Zaïre. The whole, dried, finely pulverized seeds (110 g) were successively extracted in a Soxhlet with petrol (30–80°), Et_2O and EtOH. After evapn, the petrol extract (6.5 g) afforded a yellow solid (150 mg) which was purified by column chromatography over Si gel (Me_2CO gradually added to C_6H_6) and cryst. (25 mg) from abs. EtOH. The Et_2O and EtOH extract concentrates (1.5 and 3.9 g, respectively), when submitted to analytical TLC (toluene–Me_2CO, 4:1), showed almost identical compositions. Prep. TLC of these mixtures afforded several products but the main constituent (120 mg) was identical with that isolated from petrol: mp 153–4°, mmp undepressed, analytical TLC and co-TLC (R_f 0.51). This compound appeared as a dark spot in UV light (254 nm), gave an intense yellow colour with 5% H_2SO_4–EtOH spray after 10 min at 100° but no ferric chloride reaction.

Acknowledgements—The author thanks Mrs N. Toussaint-Depaye for her valuable technical assistance, Mr J. Denoel for NMR measurements, and Dr C. Delaude and H. Breyne for collecting seeds of *Tephrosia barbigera*. The present research was performed under the auspices of the 'Centre d'études des substances naturelles d'origine végétale' at the University of Liège, in co-operation with the Belgian State (Ministère de la coopération au développement).

REFERENCES

1. Vleggar, R., Smalberger, T. M. and Dewaal, H. L. (1972) *Tetrahedron Letters* 703.
2. Smalberger, T. M., Van Den Berg, A. J. and Vleggar, R. (1973) *Tetrahedron* **29**, 3099.
3. Smalberger, T. M., Vleggar, R. and Weber, J. C. (1974) *Tetrahedron* **30**, 3927.
4. Smalberger, T. M. Vleggar, R. and Weber, J. C. (1975) *Tetrahedron* **31**, 2297.
5. Sarin, J. P. S., Singh, S., Garg, H. S., Khanna, N. M. and Dhar, M. M. (1976) *Phytochemistry* **15**, 232.
6. Krupadanam, G. L. D., Sarma, P. N., Srimannarayana, G. and Subba Rao, N. V. (1977) *Tetrahedron Letters* 2125.

7. Schwarz, J. S. P., Cohen, A. I., Ollis, W. D., Kaczka, E. A. and Jackman, L. M. (1964) *Tetrahedron* **20,** 1317.
8. Highet, R. J. and Highet, P. F. (1967) *J. Org. Chem.* **32,** 1055.
9. Vilain, C. and Jadot, J. (1975) *Bull. Soc. R. Sci. Liège* **44,** 306.
10. Vilain, C. and Jadot, J. (1976) *Bull. Soc. R. Sci. Liège* **45,** 468.
11. Vilain C. (1978) Doctoral dissertation, Liège.
12. Markham, K. R. and Mabry, T. J. (1975) in *The Flavonoids* (Harborne J. B., Mabry T. J. and Mabry H., eds.). Chapman & Hall, London.
13. Stamm, O. A., Schmid, H. and Buchi, J. (1958) *Helv. Chim. Acta* **41,** 2006.

Phytochemistry, 1980, Vol. 19, pp. 989–991. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0501-0989 $02.00/0

STRUCTURE COMPLETE DE LA RAUCAFFRINOLINE ET FILIATION AVEC LA VOMILENINE

FRANCINE LIBOT, NICOLE KUNESCH et JACQUES POISSON

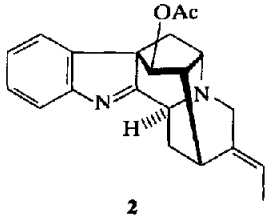
Centre d'Etudes Pharmaceutiques-F 92290 Chatenay-Malabry E.R.A. au C.N.R.S. n° 317, France

(*Recu le* 23 *juillet* 1979)

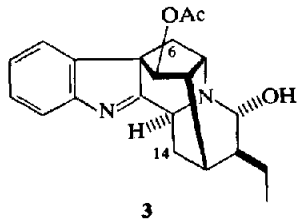
Key Word Index—*Rauwolfia* of New Caledonia; Apocynaceae; alkaloids; raucaffrinoline; vomilenine.

Les Rauwolfias de Nouvelle-Calédonie forment un ensemble taxonomique homogène [1]. L'étude chimique, qui n'avait pas été abordée jusqu'ici est en cours dans notre laboratoire [2]. En particulier, des feuilles de différentes espèces: *Rauwolfia balansae* ssp. *balansae* Boiteau, *R. balansae* ssp. *schumanniana*, var. *basicola* Boiteau, R. *spathulata* Boiteau et R. *sevenetii* Boiteau ont été isolés quatre alcaloïdes indoléniniques à squelette 'ajmaline'. Deux d'entre eux ont été antérieurement signalés dans d'autres Rauwolfias, la vomilénine **1** [3] et la desméthyl-1, deshydro-2 tétraphyllicine **2** [4, 5]. Le troisième est la desméthyl-1, deshydro-2, acétyl-17 ajmaline **3**, qui peut être préparée par oxydation de l'ajmaline **6** [6] mais qui est obtenue ici pour la première fois à l'état naturel. Enfin, le quatriéme est identique à la raucaffrinoline, alcaloïde précédemment isolé de *R. caffra* [7]: F. 249–251°, $[\alpha]_D$ +11° ($CHCl_3$) UV λ_{max} nm (log ε): 222 (4,25), 228 (4,15), 260 (3,66).

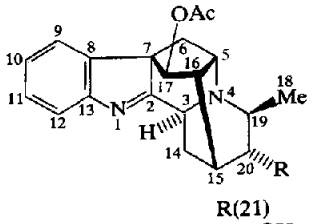
La structure **4** de la raucaffrinoline est connue, mais incomplètement définie du point de vue stéréochimique [7]. Elle dérive de celle de la vomilénine **1** via la pérakine **5** (Schéma 1). Cette conversion n'affecte pas les centres 3,5,15,16 et 17 dont la configuration est la même pour les trois alcaloïdes. Elle est reproductible *in vitro* par chauffage de la vomilénine **1** en milieu acide qui fournit la pérakine **5** [3–5] dont la réduction douce aboutit à la raucaffrinoline **4** [4, 5].



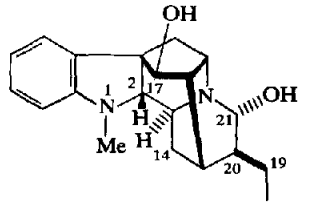
2



3



		R(21)
4A	Raucaffrinoline	CH_2OH
4B		CH_2OAc
5	Pérakine	CHO



6

7 Configurations inverses en 20, 21