Phytochemistry, Vol. 22, No. 7, pp. 1663–1664, 1983.
Printed in Great Britain.

0031-9422/83 $3.00+0.00

FLAVONOIDS AND ISOFLAVONOIDS FROM *ZOLLERNIA PARAENSIS*

F. FERRARI*, B. BOTTA and R. ALVES DE LIMA†

Centro Chimica dei Recettori e delle Molecole Biologicamente Attive del C. N. R., Università Cattolica, Via Pineta Sacchetti, 644, 00168 Roma, Italy; †Departamento de Quimica, U. F. A. L., 57.000 Maceiò, Brazil

(*Received* 7 *September* 1982)

Key word Index—*Zollernia paraensis*; Leguminosae–Papilionoideae; flavonoids; isoflavonoids; α-2′,4,4′-tetrahydroxydihydrochalcone.

Abstract—The wood of *Zollernia paraensis* contains (+)-medicarpin, (+)-vestitol, isoliquiritigenin, formononetin, (±)-7-hydroxy-4′-methoxyisoflavanone, (±)-liquiritigenin and (+)-α-2′,4,4′-tetrahydroxydihydrochalcone.

INTRODUCTION

The tribe Swartieae is a rich source of isoflavonoids: pterocarpans prevail in *Swartia* and *Aldina*, isoflavones in *Cordyla* and *Mildebraedeodendron*. The pterocarpans are phytoalexins with potential utilization as antifungal agents [1]. In the present investigation we have examined the flavonoid content of *Zollernia paraensis*, which belong to a genus not yet studied chemically. Since the heartwood of *Zollernia* is known for its durability, pterocarpans were thought to be present.

Six already known flavonoids and isoflavonoids and a new dihydrochalcone, **1**, whose structure was established as α-2′,4,4′-tetrahydroxydihydrochalcone, were isolated. Up to now only three α-hydroxydihydrochalcones, namely nubigenol [2], lyogenin [3] and α-2′-dihydroxy-4,4′-dimethoxydihydrochalcone [4] and two *C*-glucosyl derivatives, coatlines A and B [5], have been found in nature. The structure of **1** was determined on the basis of spectroscopic data and confirmed by synthesis [4] of the methyl ether, **2**, prepared via the epoxide, **3**.

Dihydrochalcone **1** and medicarpin showed a marked activity against the fungus *Cladisporium cucumerinum* by TLC bioassay.

RESULTS AND DISCUSSION

(+)-Medicarpin [6], formononetin [7], (±)-7-hydroxy-4′-methoxyisoflavanone [8], (+)-vestitol [9], (±)-liquiritigenin [10] and isoliquiritigenin [11] were identified by comparison of mp and spectra with published data.

A new compound, $C_{15}H_{14}O_5$, **1**, was also isolated. The ^1H NMR spectrum (CD_3COCD_3) was quite similar to that of (±)-liquiritigenin. It was consistent with the presence of two aromatic rings: the former 1,2,4-trisubstituted, the latter *para*-disubstituted, and a complex ABX system, reminiscent of a flavanone. The UV spectrum seemed to confirm this hypothesis. In the mass spectrum a peak at *m/z* 256 (11 %) was attributed to the M^+ of a 7,4′-dihydroxyflavanone. A doubtful result was obtained when a bathochromic shift in the UV spectrum was caused by addition of aluminium chloride. Moreover, elemental analysis gave unsatisfactory results for $C_{15}H_{12}O_4$. The product was, therefore, subjected to chemical transformations.

Methylation with dimethyl sulphate gave, surprisingly, a trimethyl derivative whose IR spectrum still exhibited strong hydroxyl absorption. Moreover, mild acetylation yielded a triacetyl derivative where one of the acetyl groups is linked to an alcoholic oxygen. A chelated hydroxyl is also present (^1H NMR evidence). Finally, examination of the mass spectrum revealed the presence of a small peak (*ca* 0.5 %) at *m/z* 274, corresponding to a molecular formula, $C_{15}H_{14}O_5$, in good agreement with the elemental analysis results (see Experimental).

All the new spectroscopic data support the α-hydroxydihydrochalcone structure, **1**. Notably, the coupling constants of the ABX system in the ^1H NMR spectrum of **1** show a close accordance with those of the same system in coatlines A and B [5]. In the literature, α-hydroxy-2′,4,4′-trimethoxydihydrochalcone, **2**, is described. The synthesis of this substance [4] was repeated by us, as in Scheme 1. The final product, $C_{18}H_{20}O_5$, was coincident in all respects with the trimethylether of **1**.

EXPERIMENTAL

Mps were determined with a Kofler apparatus and ^1H NMR Spectra at 60 MHz (TMS int. standard). Kieselgel 60 (Merck) was used for TLC and CC.

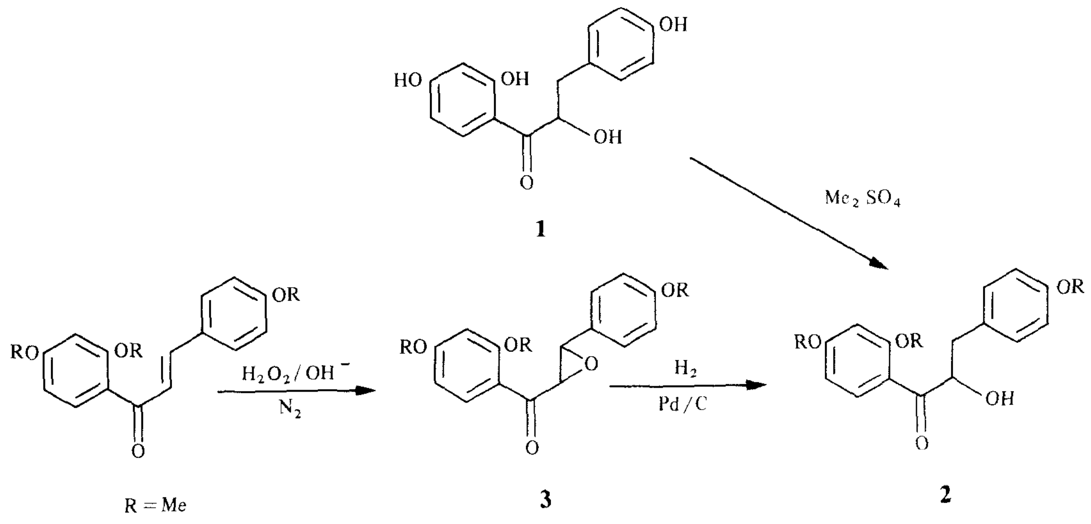
Plant material. Z. paraensins Hub. is a tall (15–20 m) tree growing in north-eastern Brazil; it was collected in Pacatuba, Cearà State, Brazil, where it is popularly named 'Coraçao de negro'.

Extraction and separation. The wood was powdered and extracted with EtOH (250 g). The syrup was extracted again with $CHCl_3$ and evaporated (50 g). The flavonoids were separated on a Si gel column using a $CHCl_3$–MeOH gradient elution system. The flavonoid content of the $CHCl_3$ extract was (+)-medicarpin (6 %), (±)-7-hydroxy-4′-methoxyisoflavanone (2.5 %), formononetin (2.5 %), (+)-vestitol (1.5 %), isoliquiritigenin (2 %), (±)-liquiritigenin (1.5 %) and α-2′,4,4′-tetrahydroxydihydrochalcone (0.4 %).

(+)-*α-2′,4,4′-Tetrahydroxydihydrochalcone* (**1**). Mp 174–177° from EtOH–H_2O; $[\alpha]_D^{20}$ + 59° (MeOH; *c* 0.18); UV λ_{max}^{MeOH} nm:

---

*To whom correspondence should be addressed.



Scheme 1.

316, 280, 225; $\lambda_{\max}^{\mathrm{NaOMe}}$ nm: 335, 240, 223; $\lambda_{\max}^{\mathrm{AlCl_3}}$ nm: 354, 281, 250, 225; ^{1}H NMR [60 MHz $(CD_3)_2CO$]: δ2.5–3.5 (2H, *m*, β), 5.17 (1H, *dd*, J = 5 and 7 Hz, α), 6.40–6.50 (2H, *m*, H-3′, H-5′), 6.70 (2H, *d*, J = 8 Hz, H-3, H-5), 7.03 (2H, *d*, J = 8 Hz, H-2, H-6), 7.90 (1H, *d*, J = 8 Hz, H-6′); EIMS (probe) 70 eV, *m/z* (rel. int.): 274 $[M]^+$ (0.5), 256 $[M-H_2O]^+$ (11), 168 (13), 137 (100), 107 (95). (Found: C, 65.81; H, 5.22. $C_{15}H_{14}O_5$ requires: C, 65.69; H, 5.15%.)

α-Hydroxy-2′,4,4′-trimethoxydihydrochalcone (**2**). Mp 61–63° from MeOH; UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm: 310, 270, 230; $\lambda_{\max}^{\mathrm{NaOMe}}$ nm: 310, 270, 230; ^{1}H NMR (60 MHz $CDCl_3$): δ2.4–3.2 (2H, *m*, β), 3.76, 3.88, 3.92 (9H, 3*s*, 3 × OMe), 5.30 (1H, *m*, α), 6.50–6.62 (2H, *m*, H-3′, H-5′), 6.80 (2H, *d*, J = 8.8 Hz, H-3, H-5), 7.10 (2H, *d*, J = 8.8 Hz, H-2, H-6), 7.90 (1H, *d*, J = 8.8 Hz, H-6′). EIMS (probe) 70 eV, *m/z* (rel. int.): 316 $[M]^+$ (1), 298 $[M-H_2O]^+$ (20), 287 (2), 283 (2), 195 (33), 167 (60), 166 (30), 165 (100), 152 (3), 139 (15); IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 3440–3480 (OH), 1655 ($>C=O$).

2′-Hydroxy-α,4,4′-triacetoxydihydrochalcone. Mp 90–93° from EtOH; UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm: 315, 275, 225; $\lambda_{\max}^{\mathrm{NaOMe}}$ nm: 335, 285 sh, 245; ^{1}H NMR [60 MHz $(CD_3)_2$ CO]: δ 2.0, 2.20, 2.26 (9H, 3*s*, 3 × OAc), 3.00–3.80 (2H, *m*, β), 6.10 (1H, *dd*, J = 5 and 7 Hz, α), 6.70–6.80 (2H, *m*, H-3′, H-5′), 6.93 (2H, *d*, J = 8 Hz, H-3, H-5), 7.35 (2H, *d*, J = 8 Hz, H-2, H-6), 8.15 (1H, *d*, J = 8.8, H-6′), 12.00 (1H, *s*, OH).

Acknowledgements—We are grateful to A. Santi (Institute of Organic Chemistry, University of Rome) for MS.

REFERENCES

1. Wain, R. L. (1977) *Semaine d'étude sur le theme 'Produits natura les et la Protection des Plantes'* 12–23 October 1976, (Marini Bettolo, G. B., ed.) Città del Vaticano, Pontificia Academia Scientiarum.
2. Bhakyni, D., Bittner, M., Silva, M. and Sammes, P. G. (1973) *Phytochemistry* **12**, 2777.
3. Shukla, Y. N., Tandon, J. S. and Dhar, M. M. (1973) *Indian J. Chem.* **11**, 720.
4. Barend Bezuidenhoudt, C. B., Vincent Brandt, E. and David Roux, C. (1981) *J. Chem. Soc. Perkin Trans.* 1, 263.
5. Beltrami, E., De Bernardi, M., Fronza G., Mellerio, G., Vidari G. and Vita-Finzi, P. (1982) *Phytochemistry* **21**, 2931.
6. Harper, S. H., Kemp, A. D. and Underwood W. G. E. (1965) *Chem. Ind.* **27**, 562.
7. Bradbury, R. B. and White, D. E. (1951) *J. Chem. Soc.* 3447.
8. Alaide de Oliveria, B., Iracema, M., Madruga, L. M. and Gottlieb, O. R. (1978) *Phytochemistry* **17**, 593.
9. Gottlieb, O. R., Alaide de Oliveira, B., Machado Goncalves, T. M., de Oliveira, G. G. and Pereira, S. A. (1975) *Phytochemistry* **14**, 2495.
10. Wong, E., Mortimer, P. I. and Geissman, T. A. (1965) *Phytochemistry* **4**, 89.
11. Clark-Lewis, J. W. and Porter, L. J. (1972) *Aust. J. Chem.* **25**, 1943.