Phytochemistry, Vol. 26, No. 8, pp. 2425–2426, 1987.
Printed in Great Britain.

0031-9422/87 $3.00 + 0.00
Pergamon Journals Ltd.

A NEW PTEROCARPAN FROM THE ROOTS OF *TEPHROSIA HILDEBRANDTII*

W. LWANDE,* M. D. BENTLEY,† C. MACFOY, F. N. LUGEMWA,† A. HASSANALI and E. NYANDAT

The International Centre of Insect Physiology and Ecology (ICIPE), P.O. Box 30772, Nairobi, Kenya; †Department of Chemistry, University of Maine, Orono, Maine 04469, U.S.A.

(*Received* 14 *January* 1987)

Key Word Index—*Tephrosia hildebrandtii*; Leguminosae; pterocarpan; hildecarpidin; isoflavonoid.

Abstract—A new 6a-hydroxylated pterocarpan has been isolated from the roots of *Tephrosia hildebrandtii* and its structure established on the basis of its spectral data.

INTRODUCTION

Tephrosia hildebrandtii Vatke is one of over 300 species of the large genus *Tephrosia* Pers that are distributed in the tropical and subtropical regions of the word [1]. We have previously reported on studies of the roots of *T. hildebrandtii* in which we have isolated hildecarpin (**1**), a new 6a-hydroxypterocarpan with insect antifeedant and antifungal properties [2, 3], four new β-substituted flavans [4] and two 8-C-prenylated flavones [5]. This paper reports on the isolation and identification of a further new 6a-hydroxypterocarpan from the roots of *T. hildebrandtii* that we have named hildecarpidin.

RESULTS AND DISCUSSION

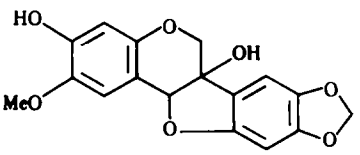
Hildecarpidin was isolated from the methanol extract of the roots of *T. hildebrandtii* as described in the experimental section. Hildecarpidin, $C_{21}H_{18}O_7$, showed spectroscopic data (UV, IR, NMR and MS) that were compatible with a pterocarpan structure. The formation of UV bands at λ346 and 363 nm on addition of HCl to the ethanolic solution of hildecarpidin and the [M − 18] fragmentation ion in its mass spectrum at *m/z* 364 were indicative of a 6a-hydroxyl group in hildecarpidin [6].

Hildecarpidin showed certain ^{1}H NMR features which were similar to those of hildecarpin (**1**) [2, 3] (Table 1); singlets at δ6.78 (1H) and 6.37 (2H) due to the H-7, 10 and 4 aromatic protons; doublets at δ3.94 and 4.14 due to the H-6 ax/eq protons, a singlet at δ5.21 due to the H-11a proton and doublets at δ5.88 and 5.92 due to a methylenedioxy group. Unlike **1**, the H-1 proton singlet was more downfield at δ7.22 and the singlet due to the methoxy group was absent. Hildecarpidin also exhibited doublets of doublets at δ3.08 and 3.34, a triplet at δ5.32 and broad singlets at δ5.23 and 4.22 indicative of the H-12, 13, 15 and 16 protons of a 2-prop-1-en-3-ol-dihydrofuran moiety attached at the C-2 and C-3 positions. Presence of the CH_2OH group in the 2-prop-1-en-3-ol-dihydrofuran moiety was substantiated by the ^{13}C NMR signal at δ61.71 and by the [364 − CH_2OH] peak in the mass spectrum at *m/z* 333. The downfield position of the H-1 proton singlet (δ7.22) indicated absence of oxygenation at the C-2 position. Hildecarpidin also exhibited a large negative optical rotation value ($[\alpha]_D$ −237 at 589 nm) and could thus be assigned the 6aS:11aS absolute configuration [7]. On the basis of the above considerations, hildecarpidin was assigned the structure **2**.

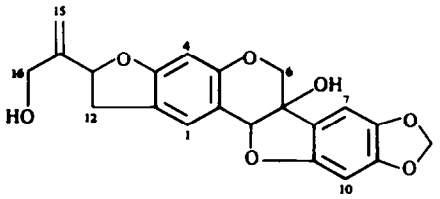
EXPERIMENTAL

Plant material. The roots of *Tephrosia hildebrandtii* Vatke were collected from Kilimambogo (Kenya) and identified at the University of Nairobi. A voucher specimen is deposited at the herbarium of the University of Nairobi under the cipher 2418.

Extraction and fractionation. Air-dried finely ground roots (1.22 kg) were extracted with cold MeOH. The evaporated MeOH extract (69 g) was partitioned between H_2O and $CHCl_3$ and the $CHCl_3$ fraction partitioned further between hexane and a MeOH–H_2O (4:1) mixture. Evaporation of MeOH from the MeOH–H_2O fraction and subsequent extraction of the residue



1



2

*Author to whom correspondence should be addressed.

Table 1. ^{1}H NMR data for hildecarpin 1 [2, 3] and hildecarpidin 2*

Proton	Hildecarpin 1	Hildecarpidin 2
H-1	6.89 *s*, 1H	7.22 *s*, 1H
H-4	6.51 *s*, 1H	6.37 *s*, 1H
H-6ax/eq	3.90 *d*, 4.13 *d*, 2H (J = 11.4 Hz)	3.94 *d*, 4.14 *d*, 2H (J = 11.8 Hz)
H-7	6.78 *s*, 1H	6.78 *s*, 1H
H-10	6.38 *s*, 1H	6.37 *s*, 1H
H-11a	5.21 *s*, 1H	5.21 *s*, 1H
H-12	—	3.08 *dd*, 1H (J = 15.6, 8.1 Hz)
H-12	—	3.34 *dd*, 1H (J = 15.6, 9.1 Hz)
H-13	—	5.32 *t*, 1H (J = 8.6 Hz)
H-15	—	5.23 *br s*, 1H
H-16	—	5.22 *br s*, 1H
MeO-2	3.88 *s*, 3H	—
O–CH_2–O	5.89 *d*, 5.93 *d*, 2H (J = 1.0 Hz)	5.88 *d*, 5.92 *d*, 2H (J = 1.6 Hz)

*Chemical shifts in values relative to TMS; solvent $CDCl_3$; 200 MHz.

with $CHCl_3$ yielded a gummy extract (12.6 g). Purification of this extract by column and preparative TLC on silica gel using an EtOAc–$CHCl_3$ gradient (2–100%) and toluene–EtOAc (4:1), respectively, as eluents afforded hildecarpidin 2 (51 mg), R_f 0.17 ($CHCl_3$–EtOAc, 4:1).

Hildecarpidin 2. 4′,5′-Dihydro-6a-hydroxy-5′-(3-hydroxyprop-1-en-2-yl)-8,9-methylenedioxy-furano[2′,3′ : 3,2]pterocarpan. $[\alpha]_D$ – 237° (1.45; *c* MeOH); UV λ_{max}^{EtOH} nm: 205, 238 (sh), 286, 320 (sh), 348 (sh), $\lambda_{max}^{EtOH+HCl}$ nm: 205, 240 (sh), 284, 310 (sh), 346, 363 (sh); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610, 3475, 1618, 1605, 1595, 1510, 950, 880; ^{1}H NMR, see Table 1; ^{13}C NMR (50 MHz, $CDCl_3$): δ 33.1 (C-12), 61.7 (C-16), 68.5 (C-6), 75.9 (C-6a), 83.4, 84.0 (C-11a, C-13), 92.9 (C-10), 97.2 (C-4), 100.3 (C-7), 101.8 (O–CH_2–O), 111.1, 111.3, 117.8 (C-6b, C-11b, C-15), 120.1 (C-2),(125.3 (C-1), 141.2 (C-8), 146.0 (C-9), 148.5, 153.2 (C-10a, C-14), 154.0 (C-4a), 159.6 (C-3); EIMS (probe) 70 eV, *m/z* (rel. int.): 382 $[M]^+$ (76), 364 $[M - H_2O]^+$ (100), 333 $[364 - CH_2OH]^+$ (84) 163 (80), 151 (47), 137 (51), 91 (46), 77 (52). (Found 382.1073, calc. for $C_{21}H_{18}O_7$: 382.1052).

Acknowledgements—W. L. is grateful to the Council for International Exchange of Scholars, Washington, DC, for a Fulbright Reseach Award, the National Science Foundation for a research grant (INT-8507043) and the Director of the International Centre of Insect Physiology and Ecology (ICIPE), Prof. Thomas R. Odhiambo, for a postdoctoral research fellowship at the University of Maine, U.S.A.

REFERENCES

1. Gillet, J. B., Polhill, R. M. and Verdcourt, B. (1971). *Flora of Tropical East Africa* (Milne-Redhead, E. and Polhill, R. M., ed.) Part 1, pp. 173. The Government Printer, Nairobi.
2. Lwande, W., Hassanali, A., Njoroge, P. W., Bentley, M. D., Delle Monache, F. and Jondiko, J. I. (1985). *Insect Sci. Applic.* **6**, 537.
3. Lwande, W., Bentley, M. D. and Hassanali, A. (1986). *Insect Sci. Applic.* **7**, 501.
4. Delle Monache, F., Labbiento, L., Marta, M. and Lwande, W. (1986). *Phytochemistry* **25**, 1711.
5. Lwande, W., Hassanali, A., Bentley, M. D. and Delle Monache, F. *J. Nat. Prod.* (In press).
6. Ingham, J. L. (1976). *Phytochemistry* **15**, 1489.
7. Ingham, J. L. and Markham, K. R. (1980). *Phytochemistry* **19**, 1203.