Pergamon

S0031-9422(96)00138-0

Phytochemistry, Vol. 42, No. 5, pp. 1473–1475, 1996

0031-9422/96 $15.00 + 0.00

A PTEROCARPAN FROM *ERYTHRINA ORIENTALIS*

HITOSHI TANAKA, TOSHIHIRO TANAKA* and HIDEO ETOH†

Faculty of Pharmacy, Meijo University, Yagoto, Tempaku-ku, Nagoya 468, Japan; *Gifu Pharmaceutical University, 6-1 Mitahora-higashi 5 chome, Gifu 502, Japan; †Department of Applied Biological Chemistry, Faculty of Agriculture, Shizuoka University, Shizuoka 422, Japan

(*Received* 2 *January* 1996)

Key Word Index—*Erythrina orientalis*; Leguminosae; isoflavones; pterocarpan; hydroxycristacarpone; 11b-hydroxydienone.

Abstract—A new pterocarpan, hydroxycristacarpone, was isolated from the wood of *Erythrina orientalis* and the structure was established as a 11b-hydroxydienone. Three known compounds, the pterocarpan, crystacarpin and the isoflavones osajin and wighteone, were also characterized.

INTRODUCTION

There have been a few reports on the chemical components and the pharmacological investigation of *Erythrina orientalis* [1, 2]. Many alkaloids have been isolated from seeds and leaves. We now report on the isolation and the structure of a new pterocarpan, hydroxycristacarpone (**1**), along with a known pterocarpan (cristacarpin (**2**) [3, 4]) and two known isoflavone's (osajin (**3**) [5] and wighteone (**4**) [6]).

RESULTS AND DISCUSSION

Compound **1**, colourless prisms, $C_{21}H_{22}O_6$, exhibited the presence of a conjugated carbonyl group (1660 cm^{-1}) in the IR spectrum. The mass spectrum of **1** showed a parent ion at *m/z* 370, 16 m.u. higher than that of **2**. In the ^1H NMR spectrum of **1**, signals of a prenyl group (δ 1.54, 1.63, 3.05, 3.18 and 5.00), a methoxyl group (δ 3.80), an oxymethylene group (δ 4.42 and 5.03), two aromatic protons (δ 6.58 and 7.21) and three olefinic protons (δ 5.265, 6.05 and 6.85) were observed (Table 1). A comparison of the ^1H NMR spectrum of **1** with that of **2** showed that substituents of ring D in **1** appeared at relatively the same positions as in **2** except for a little change in protons at 1′. Protons at 6 and 11a appeared at δ 4.42, 5.03 and 4.84, respectively. The signals of three olefinic protons exhibited a dienone system characteristic of a *p*-quinol structure in ring A. The ^{13}C NMR assignments also suggested the presence of these structural moieties. The carbons of ring A, C-1, 2, 3, 4 and 4a, were shifted downfield compared with their shift positions in **2**, whereas C-11b appeared upfield compared with its shift position in **2**.

Treatment of **1** with zinc dust in acetic acid provided **2** (6a *S* and 11a *S*) with known stereochemistry, which exhibited a negative optical rotation. Hence, **1** was concluded to have the 6a *S*:11a *R* absolute configuration. The stereochemistry of the hydroxyl group at 11b was determined by the phase-sensitive NOESY spectrum and NOE difference experiments. In the ^1H NMR spectra, two hydroxyl protons were observed at δ 5.260 and 5.68 which were assigned to 6a and 11b positions, respectively (Fig. 1). The hydroxyl proton at δ 5.68 (OH-11b) showed NOE relations with an olefinic proton at δ 6.85 (H-1) and a methine proton at δ 4.84 (H-11a) (Fig. 2). This indicated that the hydroxyl group at 11b and the methine proton at 11a had a *cis* relation. Consequently, the hydroxyl group at 11b was assigned the *S* absolute configuration and the structure of

Table 1. ^1H NMR spectral data for compounds **1** and **2**

H	1*	2†
1	6.85 *d* (10.1)	7.39 *d* (8.4)
2	6.05 *dd* (10.1, 1.7)	6.55 *dd* (8.4, 2.5)
4	5.265 *d* (1.7)	6.38 *d* (2.5)
6	4.42 *d* (10.1)	4.00 *d* (11.5)
	5.03 *d* (10.1)	4.21 *d* (11.5)
7	7.21 *d* (8.4)	7.14 *d* (8.2)
8	6.58 *d* (8.4)	6.49 *d* (8.2)
11a	4.84 *s*	5.26 *s*
1′	3.05 *dd* (14.1, 7.0)	3.25 *d* (7.3)
	3.18 *dd* (14.1, 7.5)	
2′	5.00 *m*	5.19 *br t* (7.3)
4′	1.54 *s*	1.64 *s*
5′	1.63 *s*	1.73 *s*
OMe	3.80 *s*	3.80 *s*
OH-6a	5.260 *s*	4.96 *br s*‡
OH-11b	5.68 *s*	2.37 *br s*‡

*In Me_2CO-d_6 at 400 MHz.

†In $CDCl_3$ at 270 MHz.

‡Assignments may be interchanged; OH-11b in **1** is replaced by 3-OH in **2**.

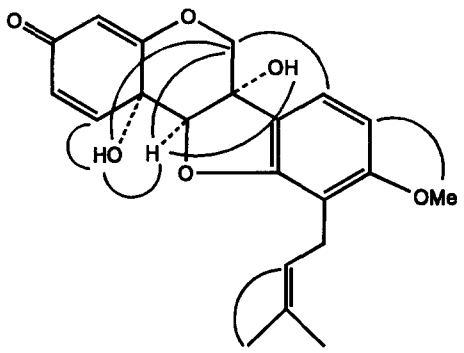


Fig. 1. NOEs observed in phase-sensitive NOESY of compound **1**.

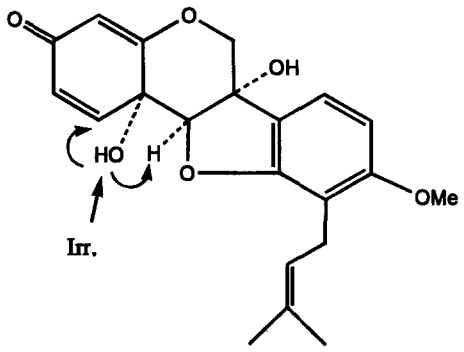


Fig. 2. Difference NOEs in compound **1**.

hydroxycristacarpone was represented as formula **1** (6a *S*, 11a *R* and 11b *S*).

So far, there have been a few reports of 11b-hydroxydienones such as derivatives of phytoalexin pterocarpans (phaseollin [7], tuberosin [8], medicarpin [9] and maackiain [9]), which are produced by oxidative detoxification of microbial alteration. The phytoalexin cristacarpin is a putative precursor of hydroxycristacarpone isolated from this plant. This is the first report of the isolation of the 11b-hydroxydienone (**1**) from the genus *Erythrina*, and hydroxycristacarpone is a rare pterocarpan which has both a prenyl group and a *p*-quinol skeleton in the structure.

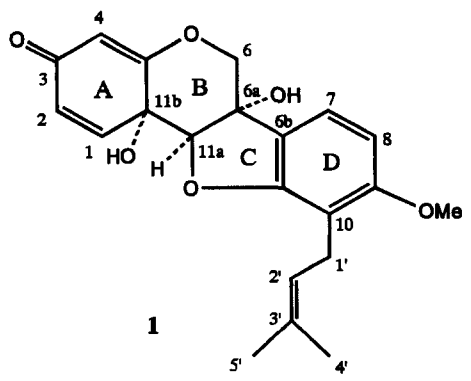
EXPERIMENTAL

Mps: uncorr. CC was run on Merck silica gel 60 (230–400 mesh). TLC was performed on glass plates precoated with Kieselgel 60 F_{254} (Merck). The spots were detected by spraying with 50% H_2SO_4 and by UV light. ^1H NMR (270 and 400 MHz) and ^{13}C NMR (67.5 MHz) spectra were measured. Chemical shifts are in ppm (δ). UV spectra were recorded in MeOH.

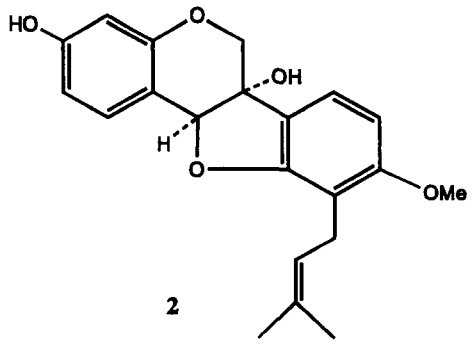
The wood of *Erythrina orientalis* (5.7 kg) was extracted with MeOH and evapd to give a dark green residue. The residue was divided into *n*-hexane soluble, CH_2Cl_2 soluble and EtOAc soluble frs. The CH_2Cl_2 soluble fr. was shaken with 2% HCl and evapd to afford an oil (11.5 g) which was chromatographed on silica gel eluted with varying polarity solns of $CHCl_3$, $CHCl_3$–Me_2CO (10:1.5) and $CHCl_3$–Me_2CO (1:1). Each fr. collected was 25 ml. Frs 97–99 were purified by repeated CC [C_6H_6–EtOAc (10:1) and *n*-hexane–Et_2O (1:1)] to afford **3** (43 mg). Frs 103–110 were sepd by CC (C_6H_6–EtOAc, 10:1) to give **2** (103 mg) and a crude solid which was recrystallized from *n*-hexane–$CHCl_3$ to give **4** (15 mg). Frs 173–180 were purified by CC ($CHCl_3$–Me_2CO, 1:1) to afford a crude solid which was recrystallized from *n*-hexane-EtOH to afford **1** (27 mg). Identification of **2**–**4** was made by comparison with lit. data [3–6].

Hydroxycristacarpone (**1**). Prisms from *n*-hexane–EtOH. Mp 246–248°. $[\alpha]_D$ −258° (MeOH, *c* 0.1). CD (MeOH; *c* 2.86×10^{-5}): $\Delta\varepsilon$ −9.74 (303), +5.73 (277), −3.97 (247). IR ν_{max}^{KBr} cm^{-1}: 3350, 1660, 1610, 1600. UV λ_{max} nm (log ε): 303 (4.64), 285 (4.75), 206 (5.64). MS *m/z*: 370 $[M]^+$, 354, 353, 340, 336, 335, 314, 297, 246, 245 (100%), 232, 231, 229, 217, 213, 205, 203, 201. HRMS *m/z*: 370.1404 ($[M]^+$, calc. for $C_{21}H_{22}O_6$: 370.1415). ^{13}C NMR (Me_2CO-d_6): δ 187.1 (C-3), 169.6 (C-4a), 160.3 (C-10a or C-9), 160.1 (C-9 or C-10a), 144.4 (C-1), 131.6 (C-3′), 129.1 (C-2), 122.7 (C-2′), 122.5 (C-7), 121.5 (C-6b), 112.5 (C-10), 107.0 (C-4), 105.2 (C-8), 90.9 (C-11a), 78.2 (C-6a), 69.9 (C-6), 68.8 (C-11b), 56.3 (OMe), 25.8 (C-5′), 22.9 (C-1′), 17.8 (C-4′). ^1H NMR: see Table 1.

Cristacarpin (**2**). Oil. $[\alpha]_D$ −187° (MeOH, *c* 0.1).



1



2

IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580, 1615, 1600. UV λ_{max} nm: 209, 280, 286. MS *m/z*: 354 ($[M]^+$, 100%), 339, 337, 336, 335, 326, 321, 311, 299, 298, 297, 295, 293, 283, 281, 271, 270, 269, 255, 217, 201. HRMS *m/z*: 354.1480 ($[M]^+$, calc. for $C_{21}H_{22}O_5$: 354.1466). ^{13}C NMR ($CDCl_3$): δ 159.8 (C-9), 158.5 (C-3), 156.9 (C-4a), 155.6 (C-10a), 132.4 (C-1), 131.8 (C-3′), 121.9 (C-2′), 120.7 (C-6b or C-7), 120.4 (C-7 or C-6b), 113.7 (C-10), 112.9 (C-11b), 110.2 (C-2), 103.9 (C-8 or C-4), 103.6 (C-4 or C-8), 84.2 (C-11a), 77.2 (C-6a), 69.5 (C-6), 56.0 (OMe), 25.8 (C-5′), 22.5 (C-1′), 17.7 (C-4′). ^1H NMR: see Table 1.

Reduction of **1**. To a soln of **1** (5.7 mg) in HOAc (2 ml) was added excess powdered Zn (20 mg). The reaction mixt. was stirred at room temp. for 30 min under N_2 atmosphere. After filtration of the reaction mixt., the solvent was evapd to give a residue which was chromatographed on silica gel using $CHCl_3$–Me_2CO (10:1.5) to afford an oil **2** (4.9 mg) which was identical to the naturally occurring cristacarpin in all respects ($[\alpha]_D$, IR, UV, MS, ^1H NMR and chromatographic properties).

REFERENCES

1. Nguyen, V. T., Pham, T. K., Hoang, T. B. Y. and Pho, D. T. (1992) *Tap Chi Duoc Hoc* 25.
2. Ito, K., Furukawa, H., Haruna, M. and Lu, S.-T. (1973) *Yakugaku Zasshi* **93**, 1671.
3. Dagne, E., Gunatilaka, A. A. L., Kingston, D. G. I., Alemu, M., Hofmann, G. and Johnson, R. K. (1993) *J. Nat. Prod.* **56**, 1831.
4. Ingham, J. L. and Markham, K. R. (1980) *Phytochemistry* **19**, 1203.
5. Mizuno, M., Matsuura, N., Iinuma, M., Tanaka, T. and Phengklai, C. (1990) *Phytochemistry* **29**, 2675.
6. Kinoshita, T., Ichinose, K., Takahashi, C., Ho, F.-C., Wu, J.-B. and Sankawa, U. (1990) *Chem. Pharm. Bull.* **38**, 2756.
7. Heuvel, J. V. D., van Etten, H. D. and Serum, J. W. (1974) *Phytochemistry* **13**, 1129.
8. Prasad, A. V. K., Singh, A., Kapil, R. S. and Popli, S. P. (1984) *Indian J. Chem.* **23B**, 1165.
9. Denny, T. P. and van Etten, H. D. (1982) *Phytochemistry* **21**, 1023.