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IDENTIFICATION OF THE *ERYTHRINA* PHYTOALEXIN CRISTACARPIN AND A NOTE ON THE CHIRALITY OF OTHER 6a-HYDROXYPTEROCARPANS

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Key Word Index—*Erythrina crista-galli*; *Psophocarpus tetragonolobus*; Phaseoleae; Leguminosae; isoflavonoids; pterocarpans; phytoalexins; absolute configuration.

Abstract—Cristacarpin, a new phytoalexin from *Erythrina crista-galli* is assigned the structure (−)-3,6a-dihydroxy-9-methoxy-10-γ,γ-dimethylallyl-*cis*-pterocarpan. It is accompanied by the known phytoalexins phaseollidin and demethylmedicarpin in this plant. Cristacarpin, phaseollidin and demethylmedicarpin were also obtained from *E. sandwicensis* and (together with isomedicarpin) from the related legume, *Psophocarpus tetragonolobus*. A compilation of selected optical rotation, NMR and conformational data for all known 6a-hydroxypterocarpans is presented and it is concluded that the previously assigned chiralities of neobanol, glyceollins I–IV and 3,6a,9-trihydroxypterocarpan should be reversed. Chirality assignments are made for a number of previously unassigned compounds.

INTRODUCTION

From comprehensive surveys undertaken in this laboratory ([1]; Ingham, unpublished), it seems possible that within the Leguminosae (subfamily Papilionoideae) production of complex pterocarpan phytoalexins may be confined to members of the Phaseoleae and closely related tribes such as the Psoraleeae. These compounds include phaseollin and phaseollidin from *Phaseolus vulgaris* and *Vigna unguiculata* amongst others [2–7], glyceollins I–IV from *Glycine max* [8, 9] and neodunol from *Pachyrrhizus erosus* [10]; all are variously prenylated, or substituted with dimethylchromen, isopropenyldihydrofuran or furan rings, features which tend to complicate structural elucidation. In some species the above compounds have been found to co-occur with simple di- or trihydroxylated pterocarpans which probably function as biosynthetic precursors [9, 10]. A recent study has revealed that fungus (*Helminthosporium carbonum*)-inoculated leaflets of the South American legume, *Eryhrina crista-galli* (coral tree; tribe Phaseoleae, subtribe Erythrininae [11]) produce a novel prenylated pterocarpan which we have named cristacarpin. The identification of cristacarpin as (−)-3,6a-dihydroxy-9-methoxy-10-γ,γ-dimethylallyl-*cis*-pterocarpan (**1**) is described in this communication.

RESULTS AND DISCUSSION

Diffusates from the *H. carbonum*-inoculated leaflets of *E. crista-galli* were found to contain substantial quantities of phaseollidin **2** (3,9-dihydroxy-10-γ,γ-dimethylallylpterocarpan) accompanied by smaller amounts of demethylmedicarpin **3** (3,9-dihydroxypterocarpan) and a third previously unreported compound (cristacarpin) which also appeared to be a pterocarpan derivative. All three compounds were absent from the control (H_2O) diffusates. The identities of pterocarpans **2** and **3** was confirmed by UV, MS and TLC comparison with authentic material.

The UV (EtOH) spectrum of cristacarpin closely resembled that of phaseollidin. Addition of aqueous NaOH led to the formation of a distinct UV maximum at *ca* 250 nm similar to that observed in the alkaline spectrum of 3-hydroxylated pterocarpans such as **2**, **3**, medicarpin [12] and 6a-hydroxymedicarpin [12]. In contrast, pterocarpans in which the 3-hydroxyl is methylated (e.g. isomedicarpin, 6a-hydroxyisomedicarpin and 2-hydroxypterocarpin [7, 12, 13]) or derivatised in some other way (e.g. neorautenol [14]) lack this alkali peak and instead exhibit a gentle shoulder between 240 and 250 nm ([12] Ingham, unpublished). With conc HCl, **1** rapidly dehydrated (see Experimental for EtOH+HCl maxima), a feature characteristic of 6a-hydroxylated pterocarpans [12, 15]. As expected, the MS (M^+ 354) exhibited a major ion at *m/e* 336 ($M^+ - H_2O$) together with other fragments at *m/e* 299 and 298 ($M^+ - 55$ and 56, respectively). The latter fragments are also evident in the MS of **2** and its dimethyl ether (**4**) and are attributed to an isopentenyl subtituent [3]. High resolution

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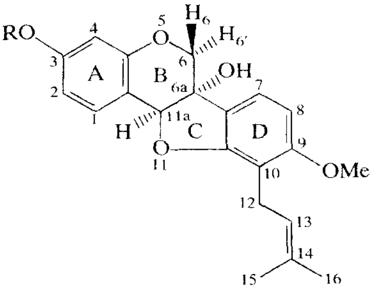
MS gave M^+ 354.1462 corresponding to $C_{21}H_{22}O_5$. Finally, upon methylation (CH_2N_2), cristacarpin yielded a monomethyl ether **5** (M^+ 368) in which the tertiary alcohol group (C-6a) was unaffected; dehydration (conc HCl) of this derivative gave a pterocarpene (λ_{max} 337 and 355 nm). In view of its co-occurrence with pterocarpans **2** and **3**, its UV (EtOH + NaOH) spectrum, and response when sprayed with diazotized *p*-nitroaniline (bright yellow, cf. **2** and **3**, orange),* cristacarpin was provisionally assigned structure **1**.



1 R = H
5 R = Me

Although cristacarpin was not obtained in quantities sufficient to permit catalytic hydrogenation [7, 8, 10], structure **1** is fully supported by ^1H NMR spectral data. The presence of single methoxyl and isopentenyl (γ,γ-dimethylallyl) substituents is readily apparent (Table 1) as also is the location of an OH group at C-6a (absence of a signal near 3.5 ppm). The A-ring substitution (C-3 OH) similarly found in other pterocarpan constituents of *E. crista-galli* is evident from the ABC pattern of aromatic proton signals typically encountered in spectra of 3-hydroxypterocarpans (see Table 1). Indeed, the chemical-shift values for H-1, H-2 and H-4 are so close to those in 3,6a,9-trihydroxypterocarpan and phaseollin (in the same solvent) and phaseollidin (in $CDCl_3$) as to exclude the possibility of a 3-methoxyl group in cristacarpin (cf. phaseollidin with isomedicarpin in which downfield shifts of 0.08 and 0.13 ppm are observed in the H-1 and H-2 signals respectively on methylation of the C-3 hydroxyl). The proposed 9,10-substitution pattern of ring D is confirmed by the *ortho*-coupled doublets at 7.18 and 6.54 ppm (H-7 and H-8) and by the absence of any signal attributable to H-10. Expected downfield shifts of H-7 and H-8 [3, 7, 16] due to methylation of the C-9 hydroxyl are evident when the NMR spectrum of **1** is compared with that of phaseollidin (in $CDCl_3$) or better, with that of 3,6a,9-trihydroxypterocarpan (in deuterated acetone) after allowing for the substituent effects of the γ,γ-dimethylallyl function at C-10 (*para*, −0.13; *meta*, −0.03 ppm [7]). The heterocyclic ring protons also exhibit chemical shifts that are in accord with those determined for other 6a-hydroxypterocarpans (Table 1).

The stereochemistry of cristacarpin may be derived from a combination of ^1H NMR and optical rotation data. Thus, since cristacarpin exhibits signals for H-6,

Table 1. ^1H NMR data for cristacarpin and related pterocarpans*

Compound	Aromatic protons†						B/C ring protons†			Isopentenyl protons†				
	H-1	H-2	H-4	H-7	H-8	H-10	H-6/6′	H-6a	H-11a	H-12	H-13	H-15/16	OMe	Ref.
Cristacarpin	7.33*d* (8.5)	6.56*q* (8.5, 2.3)	6.31*d* (2.3)	7.18*d* (8)	6.54*d* (8)	—	4.06*d* 4.16*d* (12)	—	5.27*s*	3.25*d* (7)	5.16*t* (7)	1.65*s* 1.76*s*	3.83*s*	—
3,6a,9-Trihydroxypterocarpan	7.30*d* (8.3)	6.55*q* (8.3, 2.5)	6.32*d* (2.3)	7.20*d* (8.3)	6.42*q* (8.1, 2.2)	6.24*d* (2)	4.02*d* 4.16*d* (11.6)	—	5.26*s*	—	—	—	—	[9]
Phaseollidin	7.37*d* (8.5)	6.53*q*	6.40*d*	6.93*d* (8.5)	6.36*d* (8.5)	—	3.63 4.21	3.54	5.44*d*	3.36*d*	5.28*t*	1.76*s* 1.81*s*	—	[3]
Phaseollin‡	7.35*d*	6.56*q*	6.36*d*	7.07*d*	6.28*d*	—	~3.63	~3.5	5.54*d*	—	—	—	—	—
Glyceollin IV	7.18*s*	—	6.40*s*	7.20*d* (8.6)	6.42*q* (8.2, 2.1)	6.25*d* (2.1)	4.01*d* 4.13*d*) (11.4)	—	5.20*s*	3.25*d* (7.2)	5.24*t* (7)	1.72*s*	3.79*s*	[9]
Isomedicarpin	7.45*d* (8)	6.66*q* (8, 2.5)	~6.4	7.10*d* (8)	~6.4	~6.4	4.24	—	5.52*d* (7)	—	—	—	3.8*s*	[7]

* Solvent, $CDCl_3$ (phaseollidin and isomedicarpin) or $(CD_3)CO$ (all other compounds).
† Chemical shifts are expressed as δ values (TMS reference); figures in parentheses refer to coupling constants (in Hz).
‡ Unpublished data supplied by L. J. Mulheirn.

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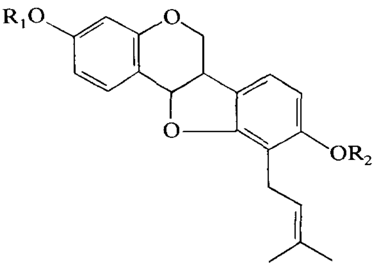
* The bright yellow colouration afforded by cristacarpin when sprayed (on TLC plates) with diazotized *p*-nitroaniline is comparable to that given by other 3,9-dioxygenated pterocarpans in which the 9-hydroxyl is blocked, e.g. medicarpin, 9-*O*-methylnissolin, phaseollin and 6a-hydroxyphaseollin [12, 23, 32, 36]. It is distinctly different from the deep orange colour afforded by related or isomeric compounds such as isomedicarpin, neorautenol and glyceollin I, which have the 9-hydroxyl free and the 3-hydroxyl blocked ([7, 14, 32]; Ingham, unpublished). The orange colour is also produced when both the 3- and 9-hydroxyls are free as in **2**, **3** and nissolin [6, 10, 36]. No exception to the '9-hydroxyl (orange)' rule has been observed.



2 $R_1 = R_2 = H$
4 $R_1 = R_2 = Me$

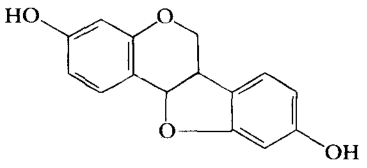


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Table 2. Physical data for known 6a-hydroxypterocarpans

Compound	$[\alpha]_\lambda$*	H-6† signal	Previously designated chirality	Reassigned‡ chirality	Reference
6a-Hydroxyphaseollin (from (−)-phaseollin)	-167°_{578}	*s*	—	6a*S*; 11a*S*	[23, 28]
6a,7-Dihydroxyphaseollin (from (−)-phaseollin)	-161°_{589}	*q*	—	6a*S*; 11a*S*	[23], Ingham, unpublished
Pisatin	$+280^\circ_{578}$	*q*	—	6a*R*; 11a*R*	[15, 29]
6a-Hydroxymaackiain (from (+)-pisatin)	$+337^\circ_{589}$	*q*	—	6a*R*; 11a*R*	[30, 31]
6a-Hydroxymaackiain (from (−)-maackiain)	−ve	*q*	(6a*S*; 11a*S*)	N.C.	[18]
Variabilin	$+211^\circ_{589}$	*q*	6a*R*; 11a*R*	N.C.	[17]
Variabilin	-230°_{589}	—	—	6a*S*; 11a*S*,	[38], Ingham, unpublished
Neobanol	-246°_{589}	*s*	6a*R*; 11a*R*	6a*S*; 11a*S*	[26]
Tuberosin	$+216^\circ_{589}$	*s*	6a*R*; 11a*R*	N.C.	[22]
6a-Hydroxymedicarpin from (−)-medicarpin	−ve	—	(6a*S*; 11a*S*)	N.C.	[18]
6a-Hydroxyisomedicarpin (from (−)-medicarpin)	-218°_{589}	—	—	6a*S*; 11a*S*	[12], Ingham, unpublished
Glyceollin I	-207°_{589} $-100\,000_{242}$	*q*	6a*R*; 11a*R*	6a*S*; 11a*S*	[8, 32, 33]
Glyceollin II	$-78\,000_{243}$	*q*	6a*R*; 11a*R*	6a*S*; 11a*S*	[8]
Glyceollin III	$-79\,000_{245}$	*q*	6a*R*; 11a*R*	6a*S*; 11a*S*	[8]
Glyceollin IV	$+ve_{291}$§	*q*	6a*R*; 11a*R*	6a*S*; 11a*S*	[9]
3,6a,9-Trihydroxypterocarpan	$+ve_{287}$§	*q*	6a*R*; 11a*R*	6a*S*; 11a*S*	[9]
Cristacarpin	-220°_{589}	*q*	—	6a*S*; 11a*S*	—
Sandwicarpin	-278°_{589}	—	—	6a*S*; 11a*S*	—

* Optical rotation; figures for glyceollin I, II and III are Cotton effect maxima.
† Present as a singlet (*s*) or quartet (*q*).
‡ Reassigned on the basis of the sign of the optical rotation (see text); N.C. = no change required.
§ CD data; both compounds also exhibit a −ve peak at *ca* 240 nm (Mulheirn, L. J., personal communication).

H-6′ and H-11a with chemical shifts similar* to those of other 6a-hydroxypterocarpans (see Table 1 and refs. [9, 17, 18]), it is considered to possess the same conformation at the B/C ring junction. This conformation has always been regarded as *cis* for 6a-hydroxypterocarpans because these compounds are presumably derived from pterocarpans in which the *cis* fusion has been proven by a combination of X-ray crystallography [19], NMR and Dreiding model studies [20, 21].

Cristacarpin exhibits a negative optical rotation [*ca* −220° (0.2 mg in 1 ml MeOH at 589 nm)] and is therefore assigned the 6a*S*; 11a*S* absolute configuration depicted (**1**). As expected, its biogenetically related co-constituents, **2** in *E. crista-galli*, and **2** plus 'sandwicarpin' (6a-hydroxyphaseollidin) in *E. sandwicensis* (see below) also have marked negative rotations (−171°, −186° and −278° respectively at 589 nm); the absolute stereochemistry of these pterocarpans is thus 6a*R*; 11a*R* for **2** (both sources) and 6a*S*; 11a*S* for 'sandwicarpin'.

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* The one variable (Table 2), the equivalence or non-equivalence of H-6 and H-6′ does not equate with differences in optical rotation (Table 2) or with *cis*/*trans* ring junction alternatives (chemical shift data, e.g. [17, 22]) and is therefore presumably 'accidental' as suggested by Burden *et al.* [23]. The chemical shifts of these protons are clearly very sensitive to magnetic anisotropy effects of substituents as well as to ring-current effects of the neighbouring benzene rings (cf. 6a-hydroxyphaseollin and 6a,7-dihydroxyphaseollin [23]).

With regard to these assignments, it should be noted that in the literature there is some confusion regarding the interpretation of optical rotation data for 6a-hydroxypterocarpans. This has resulted in negatively rotating compounds being assigned both 6a*S*; 11a*S* and 6a*R*; 11a*R* absolute configurations (Table 2). Although it is well established that *cis*-pterocarpans with negative rotation possess the 6a*R*; 11a*R* configuration ([24] and refs. cited therein) it has not always been appreciated that introduction of a 6a-hydroxyl group, whilst not affecting the sign of rotation, does reverse the nominal configuration at C-6a and C-11a (as per chirality rules [25]). Thus, negative rotation indicates the 6a*S*; 11a*S* configuration in 6a-hydroxypterocarpans. Glyceollins I, II and III [8] and neobanol [26] which were reported to exhibit negative Cotton effects/rotation must therefore possess the 6a*S*; 11a*S* configurations rather than the 6a*R*; 11a*R* configurations reported. Likewise, the minor soybean phytoalexins, glyceollin IV and 3,6a,9-trihydroxypterocarpan with positive CD peaks at *ca* 290 nm (but negative CD peaks at *ca* 240 nm; Mulheirn L. J., personal communication) must also have the 6a*S*; 11a*S* configurations depicted and not the 6a*R*; 11a*R* configurations reported [9]. Reference to data in Table 2 for the 18 known 6a-hydroxypterocarpans reveals that all other examples have been correctly assigned assuming a *cis* B/C ring fusion. (+)-Pisatin and (+)-6a-hydroxymaackiain may now be regarded as 6a*R*; 11a*R* whereas (−)-6a-hydroxyphaseollin and (−)-6a,7-dihydroxyphaseollin can be assigned the 6a*S*; 11a*S* configuration.

Apart from *E. crista-galli*, cristacarpin and compounds **2** and **3** have, as mentioned earlier, been obtained from the leaflets of several other *Erythrina* species including *E. sandwicensis* which also produces at least two additional pterocarpan derivatives; these have been identified as (−)-3,6a,9-trihydroxy-10-γ,γ-dimethylallylpterocarpan ('sandwicarpin') and 9-*O*-methylphaseollidin ('sandwicensin') (Ingham, unpublished). Although phaseollidin is regularly encountered in the Phaseoleae ([1] and refs. therein, [3–7]) the only known sources of cristacarpin are *Erythrina* species and wing bean, *Psophocarpus tetragonolobus* (subtribe Phaseolinae [11]). The *H. carbonum*-inoculated stems (see Experimental) of this legume accumulate **1–3** and isomedicarpin (3-methoxy-9-hydroxypterocarpan) but not the previously reported leaf phytoalexin, 1-methoxyphaseollidin ([1, 6, 7]; Ingham, unpublished). In diffusates from *E. crista-galli*, **1** typically attains levels ranging from 7 to 12 μg/ml (based on log $\varepsilon = 3.78$ at 286 nm for **2** [27]; values for **2** and **3** were 38–51 and *ca* 4 μg/ml respectively. All three compounds could be detected by direct TLC bioassay (*Cladosporium herbarum*) of diffusate extracts although inhibition zones due to **1** and **3** were only slight compared with that of phaseollidin.

EXPERIMENTAL

UV (EtOH) spectra and all TLC separations were undertaken as previously described [34]. MS spectra were determined using either an MS-50 (**1**) or MS-12 (**2–5**) instrument [12, 34].

Plant material. Seeds of *Erythrina crista-galli* L. and *Psophocarpus tetragonolobus* (L.) DC. var. UPS 122 (supplied by the Adelaide Botanic Garden and W. Erskine, University of Papua–New Guinea respectively) were grown as previously described (*Erythrina* [35]; *Psophocarpus* [34]).

Isolation of cristacarpin and associated pterocarpans. (a) *E. crista-galli.* Extracts (EtOAc) of fungus-induced leaf diffusates [12] were chromatographed (Si gel TLC, $CHCl_3$–MeOH, 50:1) to give **2** (R_f 0.40), cristacarpin **1** (R_f 0.28) and **3** (R_f 0.16). All three compounds were eluted (EtOH) and further purified by TLC in *n*-pentane–Et_2O–HOAc, 75:25:3 (**1**, R_f 0.25; **2**, R_f 0.35; **3**, R_f 0.20). Pterocarpans **1–3** were not produced by leaflets treated with de-ionized H_2O. (b) *P. tetragonolobus.* Inoculated stem tissues [37] were excised, extracted with EtOH [37] and the solvent removed *in vacuo* (40°). Isomedicarpin (R_f 0.65) and compounds **1–3** (see above for R_f values) were obtained by TLC ($CHCl_3$–MeOH, 50:1) of the residue. Yields of **1**, **2**, **3** and isomedicarpin were 68, 371, 12 and 10 μg/g fr. wt respectively.

3,6a-Dihydroxy-9-methoxy-10-γ,γ-dimethylallylpterocarpan **1** (*cristacarpin*). Diazotized *p*-nitroaniline, yellow. Gibbs reagent, no reaction. λ_{max}^{EtOH} nm: 210(100%), 234 sh (33%), 281 (13%), 287 (14%); $\lambda_{max}^{EtOH+NaOH}$ nm: 222 (100%), 251 (50%), 280 sh (23%), 288 (27%), 299 sh (15%); $\lambda_{max}^{EtOH+HCl}$ nm: 211 (100%), 232 sh (58%), 243 sh (56%), 251 sh (48%), 276 sh (19%), 287 (25%), 320 sh (52%), 336 (86%), 354 (74%). MS *m/e* (rel. int.): 355 (24), 354 (M^+; 95), 339 (20), 337 (25), 336 (100), 335 (31), 326 (26), 321 (19), 311 (10), 299 (11), 298 (34), 297 (20), 295 (9), 293 (21), 283 (20), 281 (16). HRMS, M^+ 354.1462 ($C_{21}H_{22}O_5$). *Monomethyl ether* **5** (CH_2N_2) (R_f 0.20, $CHCl_3$–CCl_4, 2:1) λ_{max}^{EtOH} nm: 215 (100%), 232 sh (65%), 280 (27%), 286 (28%); $\lambda_{max}^{EtOH+HCl}$ nm: 212 (100%), 232 (56%), 253 sh (33%), 278 sh (24%), 286 (26%), 323 sh (40%), 337 (54%), 355 (48%); the EtOH spectrum was unaffected by addition of aq. NaOH. MS *m/e* (rel. int.): 369 (5), 368 (M^+; 22), 353 (5), 351 (24), 350 (100), 349 (27), 340 (5), 335 (15), 312 (9), 307 (15), 297 (5), 295 (7), 293 (11), 292 (21), 291 (10), 284 (10).

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