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NOVEL PTEROCARPINOIDS FROM GLYCINE SPECIES

R.L. Lyne, L.J. Mulheirn and N.T. Keen*

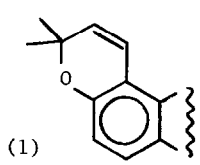
Shell Research Limited, Shell Biosciences Laboratory,
Sittingbourne Research Centre, Sittingbourne, Kent, ME9 8AG

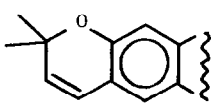
* Department of Plant Pathology, University of California
Riverside, California, U.S.A.

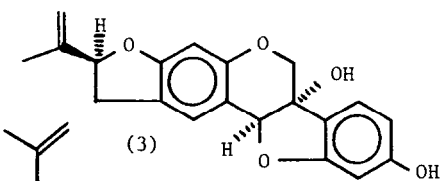
Summary : Bacteria-infected leaves of two Glycine species contain isoprenyl 6a-hydroxy-pterocarpinoids including two novel compounds canescacarpin (4) and clandestacarpin (5), for which structure and stereochemistry have been determined.

In previous reports [1,2] we described five 6a-hydroxylated pterocarpinoids produced by soybean (Glycine max (L.) Merr.) in response to fungal infection or chemical injury. Metabolites of other members of the genus Glycine have now been examined and two novel pterocarpinoids have been isolated from infected leaves of G. canescens and G. clandestina.

Extraction of leaves of G. canescens (PI 399478)[3] challenged with Pseudomonas pisi gave a fraction which, on purification by TLC and HPLC, gave three components in a 1 : 2 : 1 ratio. The less polar metabolites were identified as glyceollins I(1) and II(2). The third component crystallised from aqueous ethanol [m.p. 164-167° ; $C_{20}H_{18}O_5$ (M^+ 338.1148); λ_{max}(EtOH) 287 (8960), 292 (9210)nm]. UV, mass and CD spectra were similar to those of glyceollin III (3), though it gave a higher melting point and shorter HPLC retention time. The ^{1}H n.m.r. spectra of the two compounds were also similar, except for a small chemical shift difference observed in the d_6-benzene spectra for hydrogens at C-12 and C-13 (Table). Thus the new compound, canescacarpin, appeared to be a stereoisomer of (3), probably differing in configuration at C-13, since CD spectra indicated that both compounds have the 6aS, 11aS stereochemistry[2] *.


(1)


(2)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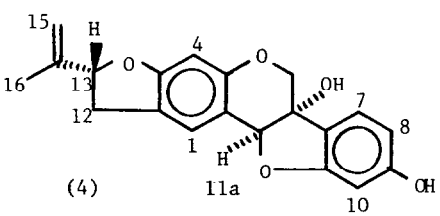
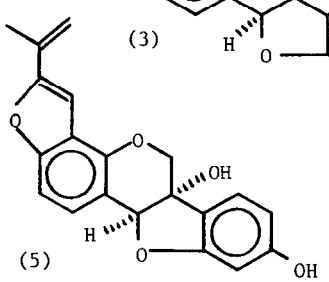

(4)


(5)

The proposed structure for canescacarpin (4) was confirmed by two experiments. Dehydration of (3) and (4) with formic acid gave the corresponding pterocarpenes. The CD spectra of the purified products (Θ_{max} (+)7,800 and (-)8,600 respectively at 247nm) confirmed that the G.canescens metabolite has the 13R configuration. This assignment was supported by treatment of (3) and (4) with osmium tetroxide-pyridine.[1] CD spectra of the resulting esters gave Cotton effects of opposite sign (Θ_{max} (+)4400 and (-)3940 respectively at 474nm).

* In refs. 1 and 2, the absolute configurations of (1)-(3) were erroneously described as 6aR, 11aR. The C-6a hydroxyl group reverses the priority of substituents relative to that of 6a-H pterocarpans.[4,5]

Infection of leaves of G. clandestina (PI 248252)[3] with P. pisi resulted in production of a single pterocarpinoid having an HPLC retention time between those of (1) and (2). Clandestacarpin [$C_{20}H_{16}O_5$; M^+ 366.0998 ; λmax (EtOH)287, 310(sh)nm] could be identified as a ring-A substituted 6a-hydroxypterocarpan from its ^1H n.m.r. spectrum and the ease of dehydration with formic acid to a pterocarpene. CD spectra confirmed the 6aS, 11aS configuration of the metabolite, while its dehydration product contained no optically active chromophore.

The 360 MHz ^1H n.m.r. spectrum (Table) confirmed the oxygenation pattern of the aromatic rings and indicated attachment of a sidechain at C-4. The broad signal at 6.80δ, assigned to a β-proton in a benzofuran ring,[6] and the presence of signals for two geminal olefinic protons and a vinyl methyl group indicated the structure of the side chain to be that of an α-substituted benzofuran, permitting assignment of structure (5) to the new metabolite.

The two new pterocarpinoids reported here have been detected in some other Glycine species. However, there is considerable variability both between and within species. For example eight strains of G.clandestina have been examined, only the first of which produces clandestacarpin. Full details of chemotaxonomic studies will be published elsewhere.

^1H n.m.r. data for phytoalexins (3) - (5)[(a)]

Proton	(3) δ	(3) J(Hz)	(4) δ	(4) J(Hz)	(5) δ	(5) J(Hz)
H_1	7.27s	-	7.22s	-	7.43d	8
H_2	-	-	-	-	7.20d	8
H_4	6.27s	-	6.22s	-	-	-
H_7	7.23d	8	7.18d	8	7.26d	8
H_8	6.46q	8,2	6.38q	8,2	6.45q	8,2
H_{10}	6.26d	2	6.23d	2	6.27d	2
H_{12}	3.05[(b)]	16,8	2.99[(c)]	16,8	6.80s	-
H_{12}'	3.42[(b)]	16,9	3.35[(c)]	16,9	-	-
H_{13}	5.26	8	5,21	8	-	-
H_{15}	4.91s[(d)]	-	4.88s[(d)]	-	5.20s[(d)]	-
H_{15}'	5.08s[(d)]	-	5.05s[(d)]	-	5.72s[(d)]	-
Me_{16}	1.77s	-	1.78s	-	2.13s[(d)]	-

(a) spectra measured in $(CD_3)_2CO$ (internal TMS) ; (b) 2.58/2.78δ in C_6D_6 ;
(c) 2.49/2.68δ in C_6D_6 ; (d) broad signal.

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