

Absolute Configuration of Pterocarpinoids

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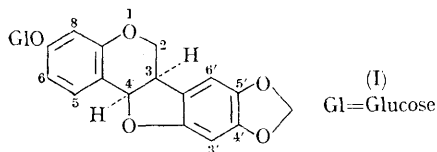
THROUGH the reaction sequence described below, we have correlated the stereochemistry of trifolirhizin (I) [(-)-maackiain- β -D-glucoside] with that of aucubin. In this way the absolute configuration of almost all known pterocarpinoids has been established.

Trifolirhizin tetra-acetate,¹ $[\alpha]_D - 137^\circ$, was

hydrogenolysed (H_2/Pd under acidic conditions) to its dihydro-derivative (II), m.p. 150° , $[\alpha]_D - 12.0^\circ$, and then ozonized (decomposition by H_2O_2) to give an oily acid (IIIa), $[\alpha]_D - 22.1^\circ$, methyl ester (IIIb), liq., $[\alpha]_D - 39.9^\circ$, ν_{max} 1785, 1738 cm^{-1} , bis-hydrazide (IV), m.p. 160° , $[\alpha]_{400} - 11.5^\circ$, $[\alpha]_{364} - 15.6^\circ$, $[\alpha]_{311} - 27.0^\circ$. (IIIa), (IIIb), and (IV)

¹ (a) J. B. Bredenberg and P. K. Hietala, *Acta Chem. Scand.*, 1961, **15**, 696, 936; (b) S. Shibata and Y. Nishikawa, *Chem. and Pharm. Bull. (Japan)*, 1963, **11**, 167; (c) Y. Fujise, T. Toda, and S. Itô, *ibid.*, 1965, **13**, 93.

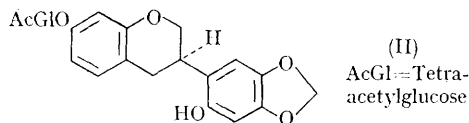
were found to be identical in all respects with (-)-paraconic acid² (resolved *via* the brucine salt)



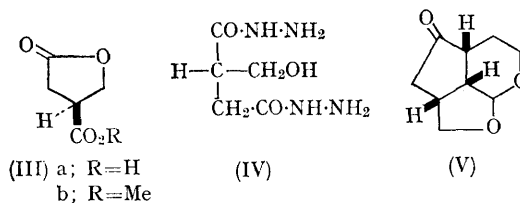
$[\alpha]_D - 60.4^\circ$, its methyl ester, $[\alpha]_D - 31.8^\circ$ and its bishydrazide, m.p. 168—169°, $[\alpha]_{253.6} - 115.0^\circ$,* respectively. Furthermore, (IV) was identical with the paraconic acid bishydrazide, m.p. 167—168°, $[\alpha]_{311} - 27.0^\circ$, $[\alpha]_{253} - 115.2^\circ$, obtained by the Baeyer-Villiger oxidation of tetrahydroanhydroaucubigenone (V) followed by a permanganate oxidation.² Since the absolute configuration of aucubin and of the paraconic acid obtained from it has been established,³ the *R*-configuration at C-3 in (I) and (II) follows from the present work.

When the known *cis*-relationship at C-3 and C-4^{5,6} in (-)-maackiain (VI)⁴ and its methyl ester (VII)^{1b} (pterocarpin) is taken into consideration, our results lead to the clarification of the complete absolute stereochemistry of (I), (VI), and (VII). Moreover, since all the known pterocarpinoids,

(+)-, (-)-, (\pm)-maackiain^{1b} (also called inermine⁷) and their glucosides, homopterocarpin,⁸ phaseolin,⁹



edulin,¹⁰ have only two asymmetric centres, at C-3 and C-4, and since the sign of optical rotation is entirely governed by the configurations at these centres. The *3R,4R*-configuration is suggested for all (-)-pterocarpinoids; the *3S,4S*-stereochemistry follows for the (+)-counterparts.



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* In Reference 2, the bishydrazide is erroneously reported to be dextrorotatory.

² S. Fujise, M. Maruyama, and H. Uda, *J. Chem. Soc. Japan*, 1962, **82**, 367.

³ H. Uda, M. Maruyama, K. Kabuki, and S. Fujise, *J. Chem. Soc. Japan*, 1964, **85**, 279.

⁴ H. Sugimoto, *Experientia*, 1962, **15**, 161.

⁵ J. B. Bredenberg and J. N. Shoolery, *Tetrahedron Letters*, 1961, 285 and the following papers.

⁶ H. Sugimoto, *Experientia*, 1962, **15**, 163.

⁷ W. Cocker, T. Dahl, C. Dempsey, and T. B. H. McMurry, *Chem. and Ind.*, 1962, 216.

⁸ E. Späth and J. Schlager, *Ber.*, 1940, **73**, 1.

⁹ I. A. M. Cruickshank and D. R. Perrin, *Life Science*, 1963, 680; D. R. Perrin, *Tetrahedron Letters*, 1964, 29.

¹⁰ B. L. Van Durren, *J. Org. Chem.*, 1961, **26**, 5013.