A CONVENIENT AND HIGHLY REGIO-SPECIFIC DEUTERIATION OF THE PTEROCARPANOID PHYTOALEXIN MAACKIAIN

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SUMMARY

A procedure is described which allows specific deuteriation at the 4-position of maackiain (3-hydroxy-8,9-methylenedioxypterocarpan) to the extent of about 30%.

Key words: Phytoalexin, Pterocarpans, ^{1}H-Nmr, ^{2}H-Nmr, ^{13}C-Nmr.

INTRODUCTION

Maackiain (= inermin) (1), believed to function as a post-infectionally produced antifungal defence agent (phytoalexin) in several Leguminosae, is one of the most commonly encountered naturally occurring pterocarpans (1-3). For biosynthetic studies which have now been discontinued, we have prepared maackiain substantially deuteriated in the 4-position by a method which may prove generally useful in the currently very active area of phytoalexin research (4).

Through the generosity of Professor Shoh Ito, we had available a quantity of trifolirhizin (2), isolated from the roots of *Ononis spinosa L.* as the tetraacetate (5), from which 1 was readily prepared by known procedures (6). Attempted deuteriation of 1 in methanol-d_4 led to no exchange in the presence of traces of acetic acid and to complete decomposition in the presence of 1% HCl even under mild conditions (32°C). Mild alkaline conditions, however, afforded maackiain which was enriched by *ca.* 30 atom % deuterium, exclusively in the 4-position. No attempts for further optimization were made.

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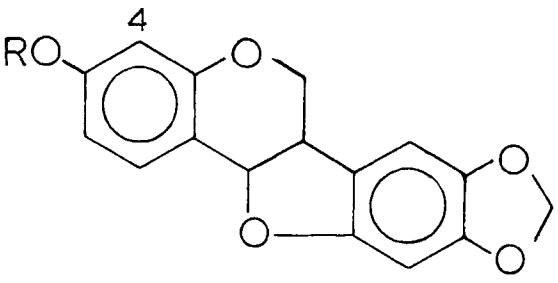

1 R = H

2 R = Gluc

METHOD AND RESULTS

A solution of 1 (29.0 mg, 1.02 mmole) in NaOH (0.10 mL, 1 M in H_2O), contained in a 5 mL glass ampoule, was diluted with D_2O (0.20 mL), evaporated under a stream of N_2 (< 60°C) and reevaporated similarly after the addition of more D_2O (0.10 mL). More D_2O (0.20 mL) was added and the ampoule was sealed. After standing at room temperature for 3 weeks, avoiding exposure to bright light, the ampoule was opened and the contents diluted with D_2O (2 mL), cooled to ice temperature, acidified (2 M HCl in H_2O, 0.1 mL) and filtered with suction. The precipitate on the filter was washed with D_2O (2 x 0.1 mL), air-dried (25.1 mg) and chromatographed over silica gel (BDH, 60-120 mesh, 5 g in light petrol) with increasing concentrations of ether in light petrol. Maackiain (19 mg) was eluted by the 30% ether fraction and was recrystallized from aqueous methanol.

Comparison of the 100 MHz proton spectra of unlabelled 1 and the deuteriated sample in $CDCl_3$ revealed differences only in the absorption bands exhibited by H-2 and H-4. For H-2, the original pattern at 6.48 ppm, a doublet of doublets (J = 8.3 and 2.5 Hz), was reduced in intensity and superimposed with a broadened doublet (J = 8.3 Hz) in the spectrum of 1-d. The doublet (J = 2.5 Hz) at 6.35 ppm for H-4 in 1, partially obscured by the singlet for H-10 at 6.38 ppm, was

significantly reduced in intensity in the spectrum of 1-d. No other differences were discernible between these two spectra and careful integration of the spectra indicated that the absorption intensity for H-4 was reduced by ca. 30% in the deuteriated sample. The 15.4 MHz deuterium spectrum of 1-d contained a single peak at 6.35 ppm. Finally, the 25.2 MHz carbon-13 spectra for 1 and 1-d were also compared and found to differ only in the relative intensity of one protonated aryl carbon, C-4, at 104.1 ppm. This signal was 30% less intense relative to those for the other protonated aryl carbons in the spectrum of 1-d. Thus, the nmr evidence confirms that deuterium exchange occurred essentially exclusively at C-4 under the reaction conditions employed.

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