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Note

Analytical separation of enantiomeric polygodials by gas chromatography of pyrrole derivatives

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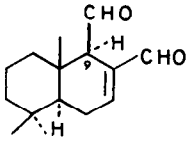
The natural drimenedial, (−)-polygodial[1,2] (1), is of strong interest by virtue of its biological activities[3,4]. The racemic dialdehyde is accessible by total synthesis[5]



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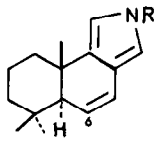

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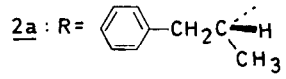

and has been resolved[6], but no productive partial synthesis of compound 1 has been reported. The phytotoxic (+)-enantiomer has to be excluded from samples of compound 1 used in biological tests[6]. We report a convenient method of analysis of the enantiomers via reactions that yield diastereomeric pyrroles. Studies of such reactions of compound 1 in aqueous media have been described earlier[3,7]. We find that polygodial (100 μg) in ethyl acetate (50 μl) at 20°C reacts very rapidly with primary amines (5 molar proportions). Gas–liquid chromatography (GLC) of an aliquot of the solution leads to conversion of the initial products[3,7] into less polar 6-enes (2) which afford good GLC peaks. The reaction products from polygodial and (−)-amphetamine showed on thin-layer chromatography (cyclohexane–ethyl acetate 70/30) spots of R_F *ca.* 0.15 and 0.42. (Vacuum sublimation yielded a new major spot, R_F 0.67, due to compound 2a.) The more polar components, on GLC , gave the same peak as compound 2a: for analytical studies, aliquots of the reaction mixtures were directly suitable. The gas chromatograms in Fig. 1 show (a) separation of derivatives formed from (±)-polygodial and (−)-*R*-amphetamine; (b) characterisation of the product (compound 2a) of treatment of a leaf extract of *Polygonum hydropiper* L. with (−)-amphetamine; and (c) complete separation of diastereomeric pyrroles

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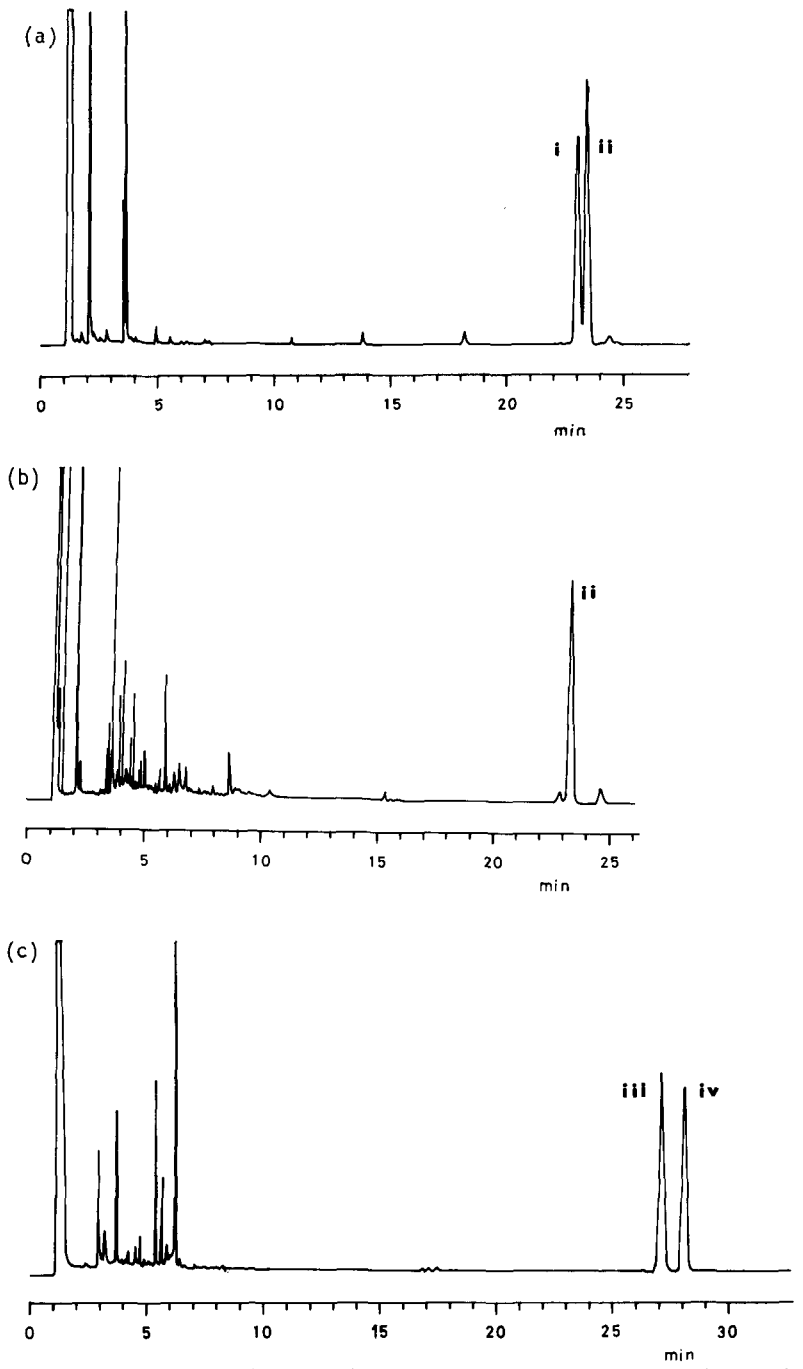

Fig. 1. Gas chromatographic traces for reaction products of polygodial with chiral amines. (a) Peak i (retention index, I, = 2475) from (+)-polygodial/(−)-amphetamine, peak ii (I = 2480) from (−)-polygodial/(−)-amphetamine; (b) reaction products from treatment of extract of mature *Polygonum hydropiper* leaf with (−)-amphetamine; (c): products of reaction of (±)-polygodial with (±)-*p*-chloroamphetamine; peak iii, I = 2664; peak iv, I = 2676 (sequence of diastereomers not yet known). Column, 25 m × 0.32 mm I.D. CP Sil 5CB (bonded phase) fused silica (Chrompack, Middelburg, The Netherlands); column temperature, 190°C (a and b), 200°C (c); helium flow-rate, 3 ml/min (flame ionisation detector).

formed from polygodial and *p*-chloroamphetamine. Mass spectra (electron impact) of diastereomers were almost identical. The reactions described show promise for precise quantitative enantiomer analysis of polygodial and related dialdehydes.

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