GLUCOSINOLATES IN TERSONIA BREVIPES (GYROSTEMONACEAE)

ANDERS KJÆR and OLAF MALVER

Department of Organic Chemistry, The Technical University of Denmark, 2800 Lyngby, Denmark

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The Australian family Gyrostemonaceae, comprising 17 species in 5 genera, has lately attracted much taxonomic interest [1]. In 1950, (+)-2-butyl isothiocyanate (2) was identified as a volatile constituent of fresh leaves of Codonocarpus cotinifolius (Desf.) F. Muell. [2], a finding to which systematic significance has been attributed in a recent discussion [1]. We report the occurrence of 2-propyl- (4), 2-butyl- (5) and 2-methylpropyl-glucosinolate (6) in seeds and leaves of Tersonia brevipes Moq., another member of Gyrostemonaceae, collected in the wild in West Australia. On myrosinasecatalysed hydrolysis, 2-propyl (1), 2-butyl (2) and 2methylpropyl isothiocyanate (3), were produced from the glucosinolate mixture in seeds as well as dried leaves, with (1), in both cases, accounting for about 90% of the isothiocyanate fraction. The enantiomeric composition of the chiral isothiocyanate (2) has not been established.

$$R-NCS$$

$$R-C \stackrel{S-Glc}{\sim} N-OSO_3$$

$$1 R = [Me]_2CH$$

$$2 R = Et(Me)CH$$

$$3 R = [Me]_2CH\cdot CH_2$$

$$6 R = [Me]_2CH\cdot CH_2$$

The finding of glucosinolates in a second member of the Gyrostemonaceae lends support to the suggested affinity of the family to those enclosed in the order Capparales [1]. It is notable that the glucosinolates encountered so far are biogenetically derived from protein amino acids, viz. valine, isoleucine and leucine, and not from their homologized counterparts (cf. ref. [3]). On this count, Gyrostemonaceae may be assigned primitive ordinal rank.

EXPERIMENTAL

GLC was performed with FID and FPD detectors; He at 20 cm/sec; programmed 50 to 250° at 8° /min, injector: 250° , detector: 280° ; SCOT SP 2100 column (42 m); split ratio 1:25; injection 0.2 μ l.

Glucosinolates. Dried fruits (seeds and capsulae) or leaves were disintegrated in CCl₄ in a Waring blendor. The residues

were extracted with hot MeOH. The extract residues were subjected to PC (Whatman No. 4) in n-BuOH-EtOH- H_2O (4:1:3) and n-BuOH-Py- H_2O (6:4:3); detection: AgNO $_3$ /NH $_3$. In both extracts only one spot was observed with R_B values (i.e. R_f values relative to that of benzylglucosinolate) of 0.60 and 0.45 in the 2 solvent systems, indistinguishable from those of authentic 4 (the other glucosinolates, 5 and 6, were present in quantities below the limit of detection).

Isothiocyanates. (a) Fruits. Dried fruits (seeds and capsulae) (46 g) were disintegrated in CCl₄ (2 × 200 ml) in a Waring blendor. The residue was suspended in a phosphate buffer (pH 6.8) (350 ml) to which a myrosinase preparation (1 ml) and a trace of ascorbic acid were added. The suspension was left for 1 hr at 35°, when H₂O (500 ml) and a trace of Triton (antifoam) were added. The suspension was subjected to extractive steam distillation in a Likens and Nickerson apparatus [4] with 2methylbutane (15 ml) as the organic phase. The dried organic soln was concd by gas entrainment at liq. N2 temp. (1 mm) to an oily residue which was applied to GLC. Among numerous components, three were singled out as S-containing by means of the FPD-detector (retention times, 9.1, 12.8, and 13.6 min; according to peak areas: 95, 3.5 and 1.5%) and identified as 1, 2 and 3, respectively, on MS comparison with authentic specimens [5]. (b) Leaves. Dried leaves (36 g) were treated similarly. The volatile fraction again contained 1, 2 and 3, yet in a slightly different ratio (89, 7 and 4%).

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