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SHORT COMMUNICATION

GLUCOSINOLATES IN TWO JAMAICAN *CAPPARIS* SPECIES

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Abstract—Glucocapparin and gluconorcappasalin have been detected in *Capparis flexuosa* L. *C. ferruginea* L. contains at least five glucosinolates and one has been shown by paper chromatography to be gluconorcappasalin.

INTRODUCTION

An extensive recent survey of many species of the Capparidaceae, but not including any from the West Indies, indicated that glucocapparin occurs frequently in several members of this family and many also contain in addition, glucocleomin.[1] To date, gluconorcappasalin has only been detected in *Capparis salicifolia* Griseb. along with its higher homologue glucocappasalin. Both De Candolle[2] and von Martius[3] place *C. ferruginea* L. in the section Calanthea. This is probably not far removed from the section Colicondendron which von Martius and Eichler[3] created for a group of Brazilian *Capparis* species and which includes *C. angulata* Ruiz et Pav. *C. angulata* contains glucocapangulin which, like glucocappasalin and gluconorcappasalin, are ketoglucosinolates. The closely related species *C. flexuosa* L. has been placed in the section Capparidastrum.[3]

RESULTS AND DISCUSSION

The isothiocyanate-producing glucosides from *Capparis ferruginea* and *C. flexuosa* were extracted into methanol and screened as outlined by Kjaer.[1] Paper chromatographic comparison of these extracts was made with several of the glucosinolates which are known to occur in *Capparis* and related species. Glucotropacolin was also used in order that R_B values could be calculated.

These experiments showed that *C. ferruginea* contained at least five glucosinolates, one of which had the identical paper chromatographic behaviour to gluconorcappasalin. These five compounds are however only present in small amounts, and one can anticipate difficulty in characterizing the other four glucosinolates by chemical means. Gluconorcappasalin was also demonstrated to be present in *C. flexuosa*, but only as a minor component. Ion-exchange chromatographic separation of the methanolic extract from *C. flexuosa* yielded a fairly homogeneous compound, which from its NMR spectrum and paper chromatographic behaviour appeared to be glucocapparin. This was confirmed by first hydrolysing this compound with myrosinase and then preparing a thiourea derivative of the liberated isothiocyanate. This derivative was shown to be identical to methyl thiourea in all respects.

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[1] A. Kjaer and H. Thomsen, *Phytochem.* **2**, 29 (1962).

[2] A. P. De Candolle, *Prodromus systematis naturalis regni vegetablis*, Part 1, p. 250. Trenttel and Würtz, Paris (1824).

[3] K. F. P. von Martius and A. W. Eichler, *Flora brasiliensis*, **13**, Parts 1 and 2. Monachii (1841–1872).

EXPERIMENTAL

Extraction

Methanolic extracts of *Capparis flexuosa* and *C. ferruginea* were prepared by disintegrating dried leaves and stems in a Waring blendor with 70 per cent (v/v) methanol.

In order to obtain known glucosinolates as reference compounds in paper chromatographic studies, seeds of *Cleome spinosa* Jacq. (glucocapparin and glucocleomin),[4] *Cochlearia officinalis* L. (glucoputranjivin and glucocochlearin),[5] *Capparis salicifolia* Griseb. (glucocappasalin and gluconorcappasalin),[6, 7] *C. angulata* Ruiz et Pav. (glucocapangulin)[8] and leaves of *C. linearis* Jacq. (3-methyl-3-butenylglucosinolate)[9] were extracted into 70 per cent methanol.

Paper Chromatography

These extracts were spotted on Whatman No. 1 paper and developed in three systems, namely, butanol: ethanol:water (4:1:4 v/v), butanol:pyridine:water (6:4:3 v/v) and butanol:acetic acid:water (4:1:5 v/v). Glucotropacolin[10] was used as an additional marker so that R_B values could be obtained. The glucosinolates were made visible on the paper by using an ammonical silver nitrate spray in the usual way.[1]

These experiments showed that *C. ferruginea* contains at least five glucosinolates, one of which was identified as gluconorcappasalin. All five glucosinolates were present only in small amounts. *C. flexuosa* also contained gluconorcappasalin as the minor glucosinolate component and the major isothiocyanate-producing glucoside appeared to be glucocapparin.

Isolation of Glucocapparin

C. flexuosa (500 g) was extracted into 70 per cent methanol (1·5 l.) and the extract concentrated to 400 ml. The glucosinolate fraction was isolated with the aid of Amberlite CG-4B (H^+).[9] The light-brown material obtained after absolute methanol treatment (2 g) gave one main spot on paper chromatograms. This material could be hydrolysed by 3 N HCl to yield hydroxylamine and sulphate ions.[11] The presence of glucose was confirmed by TLC on silica.[12] This glucosinolate compound was examined by NMR (60 Mc) in a 3:1 mixture of deuterodimethylsulphoxide and deuterium oxide and using tetramethyl-silane as reference. A sharp singlet appeared at $\delta 1{\cdot}65$ (3H; C—Me), a broad ill-defined signal was seen at $\delta 3{\cdot}12$ (1H; proton on carbon attached to —CH_2OH in glucose) and a sharp singlet appeared at $\delta 4{\cdot}31$ (6H; the other protons attached to the glucose carbon atoms).

Enzyme Hydrolysis

Myrosinase was prepared as outlined by Sandberg and Holly[13] from white mustard flour, and its activity verified by testing it on a sinigrin solution.[14] 1 g of the isolated glucosinolate was dissolved in citrate buffer (15 ml; pH 6·5). A myrosinase solution (3 ml) and a trace of ascorbic acid were added and the mixture allowed to stand 24 hr. The resulting isothiocyanate was removed by steam distillation.

Preparation of Thiourea Derivative

To the distillate 4 N methanolic ammonia was added, and the mixture allowed to stand overnight. On evaporation to dryness, a crystalline thiourea derivative (14 mg) was obtained. This thiourea was compared with an authentic sample of methylthiourea[15] prepared in the usual way from methyl isothiocyanate[16] and was shown to be identical in all respects (TLC analysis and i r.)

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