Phytochemistry, 1968, Vol. 7, pp. 131 to 133. Pergamon Press. Printed in England

GLUCOSINOLATES IN TOVARIACEAE*

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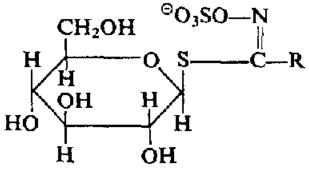
(*Received* 5 *July* 1967)

Abstract—Fresh leaves of *Tovaria pendula* Ruiz et Pavon, of the monotypic family Tovariaceae, have been established as a source of a glucosinolate, undergoing enzymatic hydrolysis to, *inter alia*, 2-propyl isothiocyanate, identified by mass-spectrometric analysis. The botanical relationship of *Tovaria* is discussed in the light of the chemical results.

INTRODUCTION

GLUCOSINOLATES, a uniform class of thioglucoside anions, (I), are typical constituents of members of the families Capparidaceae, Cruciferae, Moringaceae, and Resedaceae,[1,2] composing, together with Papaveraceae, and the monotypic families Tovariaceae and Bretschneideraceae, the order Rhoeadales *sensu* Engler and Gilg.[3]



(I)

Glucosinolates are seemingly absent in Papaveraceae, a family recently separated from Rhoeadales on botanical and biochemical evidence,[4,5] whereas little is known about their presence in the two monotypic families.

The present communication describes the results of an investigation of *Tovaria pendula* Ruiz et Pavon in this respect.

RESULTS

Paper and thin-layer chromatography of a methanolic extract of fresh leaves of *Tovaria pendula* Ruiz et Pavon† revealed the presence of one glucosinolate. In an aqueous leaf macerate this underwent enzymatic hydrolysis to give a steam-volatile isothiocyanate which

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* Part LVII of a series of papers on isothiocyanates. Part LVI: *Acta Chem. Scand.* **20**, 1778 (1966).

† Provided through the courtesy of the Botanic Garden of the University of Giessen, Germany.

[1] A. KJÆR, *Fortschr. Chem. Org. Naturstoffe* **18**, 122 (1960).

[2] M. ETTLINGER and A. KJÆR, In *Recent Advances in Phytochemistry* (edited by T. J. MABRY, R. E. ALSTON and V. C. RUNECKLES), p. 59. Appleton-Century-Crofts, New York (1967).

[3] A. ENGLER and E. GILG, *Syllabus der Pflanzenfamilien*, (9–10 Aufl.), p. 211 (1924).

[4] A. TAKHTAJAN, *Die Evolution der Angiospermen.* Fischer, Jena (1959).

[5] H. MERXMÜLLER and P. LEINS, *Botan. Jahrb.* **86**, 113 (1967).

was extracted with ether and subsequently passed, *via* a gaschromatograph, into a mass spectrometer. The molecular ion and fragmentation pattern were identical with those previously observed for 2-propyl isothiocyanate.[6, 7] The identity was further substantiated by conversion of the isothiocyanate, upon treatment with ammonia, into 1-(2-propyl)-thiourea, identified by comparison with an authentic specimen (chromatography, i.r.-spectroscopy, mixed melting point).

By chromatography, a seed extract of *T. pendula* appeared to contain the same glucosinolate as the leaves, yet in far lower concentration.

Although no rigorous proof has been furnished for the identity of the parent glucoside in *T. pendula* with glucoputranjivin (I, $R = (CH_3)_2CH$), the only formerly established progenitor of 2-propyl isothiocyanate in higher plants,[8] the identical behaviour of the two on chromatography in several solvent systems indeed suggests their identity.

DISCUSSION

Tovaria pendula, a shrub (or annual herb) indigenous to the tropical Andes region of South America, was first described by Ruiz and Pavon in 1794.[9] Endlicher[10] grouped the species together with Capparidaceae, whereas Bentham and Hooker[11] considered it rather to possess affinity to Phytolaccaceae, a relationship which has received no subsequent support. Eichler[12] included *T. pendula* in Papaveraceae, whereas Pax,[13] on the basis of certain unique morphological characters, preferred to elevate the species to family rank (Tovariaceae), a classification which, despite a proposal by Hallier[14] to merge the species with Capparidaceae, has persisted in more recent treatises.[15, 16]

In a recent survey of the occurrence of the indoleglucosinolates glucobrassicin and neoglucobrassicin, (cf. Refs. 1 and 2) in etiolated, young seedlings, Schraudolf[17] noted the presence of both in various members of Cruciferae, Capparidaceae, and (partly) in Resedaceae, as well as in *T. pendula*. In the present investigation, conducted on mature plants, no indole compounds could be detected in the latter. Glucosinolate precursors of 2-propyl isothiocyanate have been previously encountered in various families (cf. Refs. 1, 2, 18). The finding provides chemical support to the systematic alliance of Tovariaceae, not with Papaveraceae, but with Capparidaceae and associated families.

EXPERIMENTAL

A few fresh leaves of *Tovaria pendula* were placed in boiling methanol, and the extract was concentrated to a small volume. Paper chromatography of the extract, with a mixture of butanol:pyridine:water (6:4:3) as the mobile phase, and ammoniacal $AgNO_3$ as the spraying reagent, revealed the presence of only one

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[6] A. Kjær, M. Ohashi, J. M. Wilson and C. Djerassi, *Acta Chem. Scand.* **17**, 2143 (1963).

[7] E. Bach, A. Kjær, R. H. Shapiro and C. Djerassi, *Acta Chem. Scand.* **19**, 2438 (1965).

[8] A. Kjær and P. Friis, *Acta Chem. Scand.* **16**, 936 (1962), and references cited therein.

[9] H. Ruiz and J. Pavon, In *Florae peruvianae et chilensis prodromus*, **tab. 8**, p. 49 Madrid (1794).

[10] S. Endlicher, *Genera plantarum*, p. 894. Beck, Vindobonae (1836–40).

[11] G. Bentham and Hooker f., *Genera plantarum*, I, p. 110, 969. London (1862).

[12] A. Eichler, In *Flora brasiliensis* (edit. Martius) **XIII. 1**, p. 239. Fleischer, Leipzig (1889).

[13] F. Pax, In *Die Natürlichen Pflanzenfamilien* (edited by A. Engler and K. Prantl), 1. Aufl., Vol. **III.** 2, p. 207. Engelmann, Leipzig (1891).

[14] H. Hallier, In *Neue Schlaglichter auf das natürliche System der Dikotyledonen*, p. 7 Gera-Untermhaus (1905). *Beih. Bot. Centralbl.* XXXIX. 2.1, p. 39 (1921).

[15] F. Pax and K. Hoffmann, In *Die Natürlichen Pflanzenfamilien* (edited by A. Engler), 2. Aufl., Vol. **17b**, p. 224. Duncker & Humblot, Berlin (1936).

[16] J. Hutchinson, *The Families of Flowering Plants*, 2nd edn, Vol. **1**, p. 226. Clarendon Press, Oxford (1959).

[17] H. Schraudolf, *Experientia* **21**, 520 (1965).

[18] A. Kjær and H. Thomsen, *Phytochem.* **2**, 29 (1963).

glucosinolate, possessing an R_B-value* of 0·87, the same as that of an authentic sample of glucoputranjivin. On thin-layer chromatography on a cellulose plate, with the same solvent, both the *Tovaria* extract and glucoputranjivin appeared as spots with an R_f-value of 0·43.

Fresh *Tovaria* leaves (25 g fresh weight) were disintegrated, with water (75 ml), in a Waring blendor. A standard myrosinase preparation (5 ml) was added, and the mixture was set aside at room temperature for 24 hours. It was then subjected to steam distillation, and the distillate was extracted with ether and the solution dried (Na_2SO_4).

A small portion of the ether solution was applied to a gas chromatography column (2 m, 10% SE 30 on Gaschrom Z, programme 60–250°, 5°/min, inlet temperature 300°, 20 ml He/min) attached to a Hitachi–Perkin–Elmer RMU-6-D mass spectrometer (ion source 250°, ionization energy 70 eV). Apart from the solvent peak two major peaks appeared, one identified by its mass spectrum as ethyl acetate, apparently a constituent of the leaves, and the other an isothiocyanate (retention time about 6 min), easily identified by its mass spectrum as 2-propyl isothiocyanate.[6, 7]

To the remaining ether solution a saturated solution of ammonia in methanol (5 ml) was added, and the solution was kept overnight at room temperature. After evaporation to dryness, and extraction of the residue with ethanol, a crude thiourea-solution was obtained. This was purified by preparative TLC (silicagel, $CHCl_3$/EtOH 9:1, detection u.v.) to give a colourless thiourea (7·7 mg) which, after recrystallization from water, (3·5 mg), had the m.p. 169–170°, alone or in admixture with authentic 1-(2-propyl)-thiourea. The i.r. spectrum (in KBr) was indistinguishable from that of 1-(2-propyl)-thiourea, and the two samples behaved identically on TLC.

Acknowledgements—The author is grateful to Dr. H. Schraudolf for having provided the fresh plants of *Tovaria pendula*, to Dr. P. E. Brandt and A/S Grindstedværket, Brabrand, Denmark for the mass spectra, and to Mr. M. Wagnières for assistance in the experimental work.

* The R_f-value relative to that of glucotropaeolin (benzylglucosinolate).