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A NEMATICIDAL PRINCIPLE FROM THE ROOTS OF A *HELENIUM* HYBRID

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Abstract—2,3-Dihydro-2-hydroxy-3-methylene-6-methylbenzofuran, a compound with a strong nematicidal action *in vitro* was isolated from the roots of the *Helenium* hybrid 'Moerheim Beauty'.

INTRODUCTION

CULTIVATION of the *Helenium* hybrid 'Moerheim Beauty' effectively suppressed populations of plant parasitic nematodes in the soil.¹ Nematicidal principles are known from several other plants having the same effect.² A substance with nematicidal properties against several plant parasitic nematodes has been isolated from the roots of the *Helenium* hybrid and identified as 2,3-dihydro-2-hydroxy-3-methylene-6-methylbenzofuran.

RESULTS

A compound with nematicidal action, having a melting point of 75–76.5° after several recrystallizations from a mixture of diethyl ether and pentane, was isolated in 0.1% yield from the plant. The IR and NMR spectra indicated the presence of a 1,2,4-trisubstituted aromatic ring, an OH group and vinyl CH₂. Exact mass measurements indicated a compound C₁₀H₁₀O₂. The UV spectrum gave little further information on the structure of the compound. All the data obtained were in agreement with the substance being 2,3-dihydro-2-hydroxy-3-methylene-6-methylbenzofuran.

DISCUSSION

This is the first report of the isolation of a substance with nematicidal properties from roots of a member of the genus *Helenium*.

Recently a compound, for which the same structure was claimed, has been isolated from roots of other *Helenium* species.³ The presence of this compound in the roots may explain the suppressing effect of this *Helenium* hybrid on nematode populations in the soil.

EXPERIMENTAL

The *Helenium* hybrid 'Moerheim Beauty' was cultivated in the 'Kruidentuin' at Buitenpost (The Netherlands). Some roots were also supplied by Mr. Hijink.

¹ M. J. HUIJK and R. WINOTO SUATMADJI, *Neth. J. Pl. Path.* **73**, 71 (1967).

² J. H. UHLENBROEK and J. D. BIJLOO, *Recl. Trav. Chim. Pays-Bas Belg.* **77**, 1004 (1958); J. H. UHLENBROEK and J. D. BIJLOO, *Recl. Trav. Chim. Pays-Bas Belg.* **78**, 382 (1959); R. A. ROHDE and W. R. JENKINS, *Bull. Md. Agri. Exp. Stn.* A-97 (1958).

³ F. BOHLMANN, J. SCHULZ and R. BÜHMANN, *Tetrahedron Letters* 4703 (1969).

Extraction and Purification

Freshly harvested roots, stored in a freezer for 2 months, were extracted with a mixture of Et₂O and light petroleum (b.p. 40–60°) (1/2, v/v). After evaporation of the bulk of the solvent, the oily concentrate was chromatographed on a column of silica gel with petroleum with increasing quantities of Et₂O. Further purifications were carried out on thick TLC; Merck silica gel HF₂₅₄ with 40% Et₂O in petroleum (v/v) as eluent. Recrystallization was from a mixture of Et₂O and pentane; m.p. 75–76.5°.

Spectral Data

UV. λ_{\max} (pentane) 333, 328, 318, 266, 257, 228 nm. (ϵ 6800, 8000, 8900, 12,500, 14,000, 11,000).

IR (CHCl₃). OH at 3340 and 1335 cm⁻¹, vinyl 886 cm⁻¹, aromatic ring 1585 and 1439 cm⁻¹.

NMR (TMS internal standard). 1,2,4, trisubstituted aromatic ring 3.39 τ (doublet $J = 1$ c/s, 1H), 3.28 τ (double doublet $J = 1$ and 8 c/s, 1H), 2.71 τ (doublet $J = 1$ c/s, 1H); methylgroup 7.6 τ (singlet, 3H); vinyl group 4.67 τ (doublet $J = 2$ c/s, 1H), 4.49 τ (doublet $J = 2$ c/s, 1H); OH group 6.48 τ (doublet $J = 10$ c/s, 1H), H atom 3.88 τ (double multiplet, $J = 10$ c/s). Mass spectrum: M⁺ 162,0684 (calculated 162,0680).

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TRITERPENIC ALCOHOLS FROM THE SHOOTS OF *HELIANTHUS ANNUUS*

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It HAS been shown previously that great quantities of triterpenic pentacyclic alcohols of different types accumulate in the flowers and the seeds of *Calendula officinalis*. In other organs of this plant only small quantities of β -amyrin and erythrodiol, biosynthetic precursors of oleanolic acid, are present.¹ In *Helianthus annuus*, however, considerable quantities of triterpenic monols and diols were found, not only in the flowers and the seeds, but also in the shoots and the roots.² On silver nitrate-silica chromatograms these compounds had chromatographic properties identical with monols such as lupeol, taraxasterol, ψ -taraxasterol and the amyrins, and with the diols calenduladiol, faradiol, brein and erythrodiol. The chromatographic analysis of the selenium dioxide oxidation products of the amyrins revealed the presence of two compounds, one unoxidized (most probably α -amyrin) and the second one oxidized with R_f values the same as the oxidation product of β -amyrin.

The direct identification of the triterpenic alcohols present in the shoots of *Helianthus annuus* was performed by co-crystallization of the labelled compounds, isolated from this plant with unlabelled known triterpenic alcohols isolated from the flowers of *Calendula officinalis*.

3-week-old shoots of sunflower plant without cotyledons and roots, of total weight 2 g, were administered with 400 μ C ¹⁴CO₂ during 2 hr at illumination 40,000 lx. The shoots were then transferred to a vessel with tap water and illuminated with light of intensity

¹ Z. KASPRZYK and Z. WOJCIECHOWSKI, *Phytochem.* **8**, 1921 (1969)

² K. STRUBY and Z. KASPRZYK, *Acta Soc. Botan. Pol.* in press