Sesquiterpene lactones. XXXVIII. Constituents of *Picris echioides* L. and their antifeedant activity

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Abstract

Reinvestigation of components of *Picris echioides* L. led to the isolation of pure jacquinelin (I) and 8-deoxylactucin (II). The insect deterrent activities of compounds I and II, of their 1:5 mixture, as well as of the chloroform extract of *Picris echioides* were determined.

Key words: *Picris echioides*, sesquiterpene lactones, chemotaxonomy, antifeedants

INTRODUCTION

The constituents of *Picris echioides* L. have already been investigated (Bohlmann et al. 1981). Five sesquiterpene lactones: jacquinelin (I), 8-deoxylactucin (II), the 11,13-dihydro derivative of hanphyllin (IV), and the 11-epimer of jacquinelin (V) have been reported. Lactones I, II, IV and V were isolated as a mixture which was separated after acetylation. In seeking antifeedants of plant origin we investigated the chloroform extract of *Picris echioides*, as we expected to find good deterrent activity. Several sesquiterpene lactones showed marked insect feeding deterrence (Nawrot et al. 1982); having many examples of such compounds may enable us to draw conclusions on their structure: activity relationship. Our intent was to isolate the free lactones not their acetyl derivatives.

RESULTS AND DISCUSSION

The chloroform extract of *Picris echinoides* L. showed very good insect deterrent activity, when tested on four insects (see Table 1). Therefore the isolation of active principles was undertaken. Multiple chromatographies of

Table 1

The deterrent activity test (coefficients) of the sesquiterpene lactones and extract from *Picris echinoides* L.

Com- po- und	<i>Tribolium confusum</i> Duv.						<i>Trogoderma granarium</i> Ev.			<i>Sitophilus granarius</i> L.			Class*
	adults			larvae			larvae			adults			
	rel.	abs.	total	rel.	abs.	total	rel.	abs.	total	rel.	abs.	total	
I	92.0	64.1	156.1	84.2	18.1	102.3	11.0	44.9	56.0	78.6	20.7	99.3	103.4*
II	98.1	7.4	105.5	73.3	36.8	110.1	-8.7	29.0	20.3	-3.9	16.8	12.9	III 62.3*
I+II	100.0	74.9	174.9	100.0	45.8	145.8	100.0	95.6	195.6	77.2	33.3	110.5	II 156.7*
P.e.	66.0	60.3	126.3	86.7	65.9	152.6	100.0	56.7	156.7	95.9	70.9	166.8	IV 151.0*

I — Jacquinelin; II — 8-deoxylactucin; I+II — crystalline mixture of I and II; P.e. — extract of *Picris echinoides* L.

* Class — average deterrent activity of four tested insects.

Below "0" — attractant, class I (0-50) — poor deterrent, class II (51-100) — medium deterrent, class III (101-150) — good deterrent, class IV (151-200) — very good deterrent.

The following numbers of insects were used in the experiments: *Sitophilus granarius* L. — 3 adults. *Tribolium confusum* Duv. — 20 adults and 10 larvae. *Trogoderma granarium* Ev. — 10 larvae.

the chloroform extract resulted in isolation of a crystalline product which was shown by ^1H NMR to contain two sesquiterpene lactones, namely jacquinelin (I) and 8-deoxylactucin (II) (see Fig. 1). The mixture was analysed by HPLC which showed that it contained compounds I and II at a 1:5 ratio.

Fig. 1. The chemical structure of sesquiterpene lactones I and II

The biological test showed that the crystalline mixture was very good class IV deterrent for all of the insects used. Pure compounds I and II were obtained by the modified method of Pyrek (1977) and tested as antifeedants on the same set of insects. On average, 8-deoxylactucin was less active (class II) than jacquinelin (class III) and much less active than the chloroform extract. The highest activity was exhibited by the 1:5 mixture of I and II and was probably due to a synergetic effect.

EXPERIMENTAL

Picris echioides L. was grown in the garden of the Chair and Department of Medicinal Plants, Medical Academy of Poznań. The seeds were obtained from the Botanical Garden of Munich (Voucher No. 322/86). All m.ps. were measured with a Kofler block and they were not corrected. The ^1H NMR spectra were measured using a Jeol JNM 100 MHz spectrometer. The IR spectra were obtained with a Beckman Aculab spectrometer. Optical rotations were monitored by TLC. The HPLC analyses as well as semi-prep. separation Column chromatographies were carried out on silica gel Si-60 (Merck) and were monitored by TLT. The HPLC analyses as well as semi-prep. separation were performed using a Waters liquid chromatograph. Dried ground aerial parts (2.8 kg) of *Picris echioides* were extracted with chloroform and the extract was then purified by the method of Drożdż (1968).

The prepurified extract (5.2 g) was chromatographed on a column (200 g Si-gel) in a chloroform/acetone gradient system. Fractions possessing RF values 0.5-0.4 (CHCl_3 :hexane:MeOH, 45:45:10) were collected and gave a residue (0.43 g). The residue was rechromatographed on a column (25 g Si-gel) in a chloroform/acetone 9:1 solvent system and gave the main fraction which was recrystallised from a methanol-diethyl ether mixture. The crystalline product (212 mg) m.p. 151-154°C was identified by ^1H NMR as a mixture of I and II.

Separation of compounds I and II. The mixture of I and II was separated by repeated HPLC using a pack of five 8 mm i.d. 30 cm length columns filled with Lichrosorb (10 μ), joined in a series. The columns were eluted with a triple solvent system (CHCl_3 :hexane:MeOH, 48:48:4) at the rate of 5 cm³min⁻¹. The chromatography was monitored with a refractive index detector. All of the spectral and physicochemical properties of the isolated jacquinelin (I) and 8-deoxylactucin (II) were identical with those reported by Pyrek (1977).

Deterrent activity test. The test of the deterrent (antifeedant) activity of compounds I and II, their 1:5 crystalline mixture, as well as the purified extract of *Picris echioides* L. was carried out by the method of Nawrot et al. (1982) and Daniewski et al. (1988). The substances mentioned above were

tested on specimens of *Sitophilus granarius* L. (adults), *Tribolium confusum* Duv. (adults and larvae) and *Trogoderma granarium* Ev. (larvae). The results are presented in Table 1.

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Laktony seskwiterpenowe. XXXVIII. Składniki Picris echioides L. ich własności deterrentne

Streszczenie

Ponowne przebadanie zawartości ekstraktu *Picris echioides* doprowadziło do wyizolowania czystych seskwiterpenów: żakineliny (I) i 8-dezoksylaktucyny (II). Oznaczono własności deterrentne związków I i II, ich krystalicznej mieszaniny oraz ekstraktu chloroformowego otrzymanego z *Picris echioides*.