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SHORT REPORTS

MOLLUSCICIDAL ACTIVITY OF AFFININ AND OTHER ISOBUTYLAMIDES FROM THE ASTERACEAE

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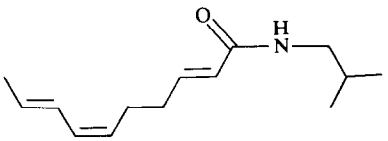
Key Word Index—*Heliopsis longipes*; *Wedelia parviceps*; Asteraceae; isobutylamines; affinin; molluscicidal activity.

Abstract—Unsaturated aliphatic isobutylamides from Asteraceae, Rutaceae and Piperaceae are potential agents to control schistosomiasis. Affinin (*N*-isobutyl-2,6,8-decatrienamide) from *Heliopsis longipes* has strong molluscicidal activity against *Physa occidentalis* (LD_{50} *ca* 100 μM) and the cercariae of the fluke. The amide has also been shown to be present in *Wedelia parviceps* flowers.

INTRODUCTION

A large number of different natural products have been shown to be effective as molluscicides and cercaricides (cercariae are the haploid forms of schistosomes which penetrate the skin of humans and cause disease) and thus are of potential use against bilharzia [1, 2]. These include sesquiterpenoid lactones of species of *Eremanthus* (Asteraceae) [3]. The efficacy of *Ambrosia maritima* L. (Heliantheae, Asteraceae) against snails has been demonstrated and ascribed to the sesquiterpenoid lactones damsin and ambrosin [4]. We now report that the unsaturated aliphatic isobutylamides (e.g. **1**) may be equally effective.



1 Affinin

RESULTS AND DISCUSSION

Isobutylamides of long-chain unsaturated acids have been long known in the Anthemideae and Heliantheae of the Compositae as well as from the Rutaceae and Piperaceae [5]. Many of these constituents are known to possess insecticidal properties [6] and to have a distinctive, somewhat pungent, taste. These components are present in all parts of the plant. For example affinin (= spilanthol, *N*-isobutyl-2,6,8-decatrienamide, **1**) is present in the roots of *Heliopsis longipes* (A. Gray) Blake [7], the leaves of *Spilanthes oleraceae* Jacq [8] and we have identified it in the flowers of *Wedelia parviceps* Blake. These three species are used in folk medicine for their analgesic effect in Mexico [9], Belize [10] and in the Far East [6], and the insecticidal uses of *H. longipes* have been noted [9].

We extracted affinin (**1**) from the roots of *H. longipes*, purified it by HPLC and tested it against the freshwater snail *Physa occidentalis* Tryon and the leptocercous cercariae of the Echinostome released by the mollusc. Above 50 mg/l. in water at 21° snails were inactive after 60 min and dead within 18 hr. At 150 mg/l. (the solubility limit for **1**) cercarial emergence ceased and the snails showed immobility after 30 min. Cercariae ceased to move after 5 sec and convulsed after 1 min. These results are comparable with those for damsin (14 mg/l. [3]) but show that the amide is probably less effective than saponins [11, 12]. The crude pulverized root of *H. longipes*, besides showing molluscicidal activity was active against fish showing the necessity to evaluate the advantages of the application of this material before use.

The presently reported distribution of the unsaturated isobutylamides in the Asteraceae is relatively restricted [13], but there seems reason to believe that they are more widespread than realized. We have shown that the flowers of *W. parviceps* contain affinin (**1**) and it seems probable that similar compounds are widely distributed in the Heliantheae.

EXPERIMENTAL

Extractions and purifications of affinin (**1**). Dried roots of *H. longipes* or flowers of *W. parviceps* were extracted exhaustively with 95% EtOH. The filtered soln was diluted with H_2O and extracted with light petrol. The residue from

the petrol extract was triturated with $CHCl_3$ and the solubles separated on Si gel with $CHCl_3$–MeOH–NH_3 [14]. Final purification was by HPLC on Micropak mCH 10 with MeCN. The amide was identified by UV spectra and retention times.

Biological assays. The compound (satd soln in H_2O, 157 mg/l.), was added at various concns to Petri dishes containing 5 snails (*Physa occidentalis* or *Lymnaea* spp: collected near Vancouver) and visual observations made of the responses. Similar tests were made with cercariae. Extracts of preserved roots of *H. longipes* were tested similarly, and against the common guppy (*Lebistes reticulatus*).

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DHURRIN, THE CYANOGENIC GLUCOSIDE OF *CERCOCARPUS LEDIFOLIUS*

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Key Word Index—*Cercocarpus ledifolius*; Rosaceae–Rosoideae; cyanogenic glucoside; dhurrin.

Abstract—Dhurrin (2-β-D-glucopyranosyloxy-2-(4-hydroxy)phenyl-2*S*-acetonitrile) was isolated as a cyanogenic compound from *Cercocarpus ledifolius* and identified by its hydrolysis products, chromatographic properties and ^1H NMR spectroscopy.

INTRODUCTION

Within the Rosaceae the phenylalanine-based cyanogenic glycosides amygdalin and prunasin are found mainly in the subfamilies Maloideae and Prunoideae [1] and hence have been considered to be the typical cyanogens of the family. However, other types of cyanogenic glycoside may occur in this family [2–4]. Recently the leucine-derived cyanogenic glucosides heterodendrin [5] and the 4-hydroxybenzoic acid ester [6] and 4-hydroxycinnamic acid ester of cardiospermin [5] have been detected in *Sorbaria* (Rosaceae–Spiraeoideae). We now describe the isolation and identification of dhurrin from *Cercocarpus ledifolius* Nutt. (Rosaceae–Rosoideae), a shrub or tree, growing in the western parts of the U.S.A. [7].

RESULTS AND DISCUSSION

Air-dried leaves and twigs of *C. ledifolius* were collected in the Sierra Nevada of northern California. The