of the pyranols **3** and **4** generated (6*S*)- and (6*R*)-tetrahydro-2,2,6-trimethyl-6-vinyl-2*H*-pyran-3-ones **9** and **10** respectively. Coinjection by chiral GC showed (6*S*)-tetrahydro-2,2,6-trimethyl-6-vinyl-2*H*-pyran-3-one **9** to be identical to the component produced by Sissinghurst Pink and Pink Parfait. In olfactometer studies, WFT were attracted to **5** but not to **3** or to a mixture of **5** and **3** in the ratio produced by Sissinghurst Pink cultivar, suggesting that there may be separate olfactory receptors for the two diastereoisomers of linalool oxide and that other components of the flower volatiles must contribute to the attractiveness of the odours from Tapien Pink and Pink Parfait.

ACKNOWLEDGEMENTS

This work was carried out with the financial support of the Ministry for Agriculture Food and Fisheries. IACR-Rothamsted receives grant-aided support from the Biotechnology and Biological Sciences Research Council of the United Kingdom.

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Developing new herbicide models from allelochemicals†

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Abstract: Plants contain allelochemicals which are their own defence systems and can act as herbicides. Selected examples of guaianolides and heliannuols, which are sesquiterpenes, are discussed in the context of their potential use as natural herbicide templates.

Keywords: Allelopathy; sesquiterpene; herbicide; bioassay; standard target species

1 INTRODUCTION

The indiscriminate use of herbicides has provoked an increasing incidence of resistance in weeds and new, more efficient and specific herbicides are needed.

Plants and micro-organisms contain allelochemicals which act as their defence system and may act as herbicides. Thus naturally occurring allelochemicals may act as templates for the synthesis of active compounds for use as herbicides[1–5] There have been several reports of the action of sesquiterpene lactones, which occur as allelochemicals in some plants, as inhibitors of plant germination and growth.[6,7] This activity has been attributed to analogues of compounds containing a methylene-γ-lactone moiety. We have isolated such compounds from the leaves of sunflowers (*Helianthus annuus* L)[8,9] and have synthesised a number of guaianolide, eudesmanolide, germacranolide, *cis,cis*-germacranolide, heliangolide and melampolide analogues.[10] As part of an on-going search for new agrochemicals based on allelopathic properties, we have synthesised some guaianolides and heliannuols based on those present as biocommunicators in selected sunflower cultivars and tested them for their ability to affect germination and root and shoot growth of some test plants.

2 EXPERIMENTAL

2.1 Compounds

Figure 1 shows a selection of sesquiterpene lactones isolated from natural sources and/or synthesised from the readily available compound dehydrocostuslactone.

2.2 Seed germination and root and shoot growth bioassays

Stock test solutions in water (10^{-3} M) of pure test compound, or of the commercial herbicide mixture terbutryn + triasulfuron (Logran, Novartis), were diluted to the appropriate concentration and adjusted to pH 6.0, using 2-(*N*-morpholino)ethanesulfonic acid. The test solution (5 ml), or a water control, was added to a sheet of filter paper contained in a Petri dish, seeds of the appropriate test plant were added and the dish was then incubated in the dark in a growth chamber at 25 °C. The test species were as follows (number of seeds and incubation time in parentheses): lettuce, *Lactuca sativa* L cvs Nigra and Roman (25; five days); tomato, *Lycopersicon esculentum* L (25; five days); onion, *Allium cepa* L (25; five days); cress, *Lepidum sativum* L (25; three days); barley, *Hordeum vulgare* L (10; five days) and wheat, *Triticum aestivum* L (10; five days). There were four replicate dishes per treatment, except for wheat and barley, which had 20 replicates. A similar number of controls incorporating seeds incubated on filter paper treated with water was included. The extent of germination, root and shoot length were recorded and subjected to Welch's test which determines differences, significant at $P = 0.01$, between the treatment and the control.

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† Part 9 in the series 'Natural Products as Allelochemicals': Part 8 – Macias FA, Simonet AM, Galindo JCG and Castellano, D, *Phytochemistry* **50**: 35–46 (1999)

Contract/grant sponsor: Secretaria General del Plan Nacional de I and D, Spain; contract/grant number: CIYCT;AGF97-1230-C02-02 (*Received 3 July 1998; accepted 17 February 1999*)

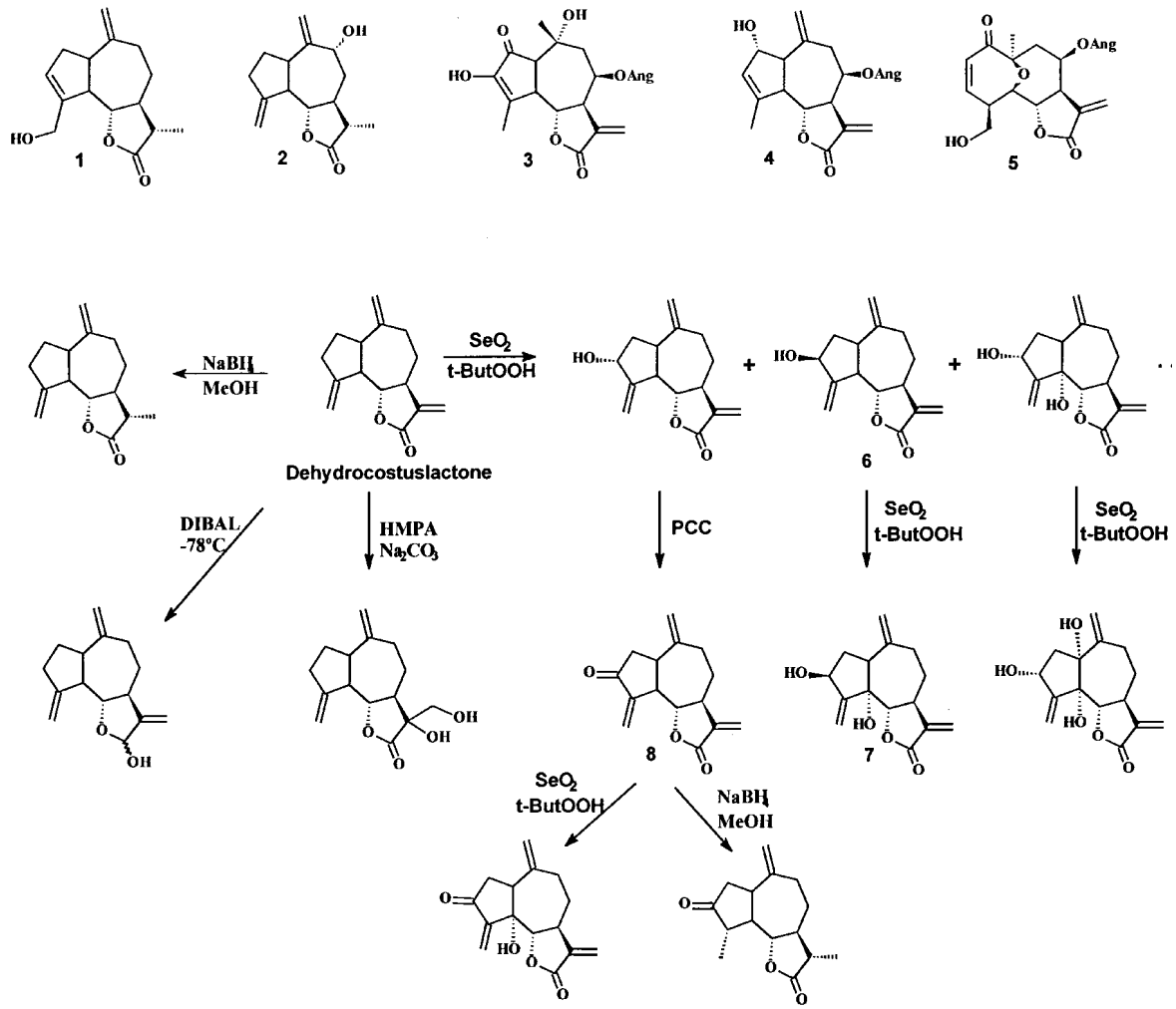

Figure 1. Sesquiterpene lactones.

3 RESULTS AND DISCUSSION

3.1 Guaianolides

Simple guaianolides such as **1** (Fig 1) strongly inhibited germination of lettuce seeds (**1** gave 71% inhibition at 10^{-5}M) but had little effect on root or shoot growth of those seeds which did germinate. However, compounds **3** and **4**, with a second α,β-unsaturated system in the form of an angeloyl ester group at C-8, stimulated germination of lettuce but inhibited root and shoot development. Compounds **3, 6,** 7 and **8** inhibited root and shoot growth in lettuce, tomatoes and cress. Results are shown graphically in Fig 2.

3.2 Heliannuols

A number of compounds of this type have been isolated from sunflowers[10] and from a marine source.[11] Synthesis routes for some heliannuols are illustrated in Fig 3. The commercial product Logran greatly inhibited germination, especially of lettuce, but this effect diminished drastically at concentrations below 10^{-6}M; inhibition of root growth of lettuce seedlings followed a similar pattern. By contrast, Heliannuol A (**9**) gave *c*40% inhibition of germination irrespective of concentration in the range 10^{-4}–10^{-9}M, ie it inhibited germination at concentrations lower than that needed with Logran. Heliannuol D (**12**) stimulated germination but inhibited root and shoot growth. Heliannuol B (**10**) did not inhibit root growth of cress but gave 38–60% inhibition of shoot development at 10^{-8}–10^{-4}M. The allelochemicals had little effect on onions apart from Heliannuol D (**12**) which produced 40–50% and 35–45% reduction in root and shoot length, respectively, at 10^{-5}–10^{-3}M, activity similar to that obtained with Logran at higher concentrations.

4 CONCLUSIONS

Some of the allelochemicals discussed here have activity profiles similar to that obtained with Logran in that they can inhibit germination and/or growth of some dicotyledonous plants while stimulating shoot

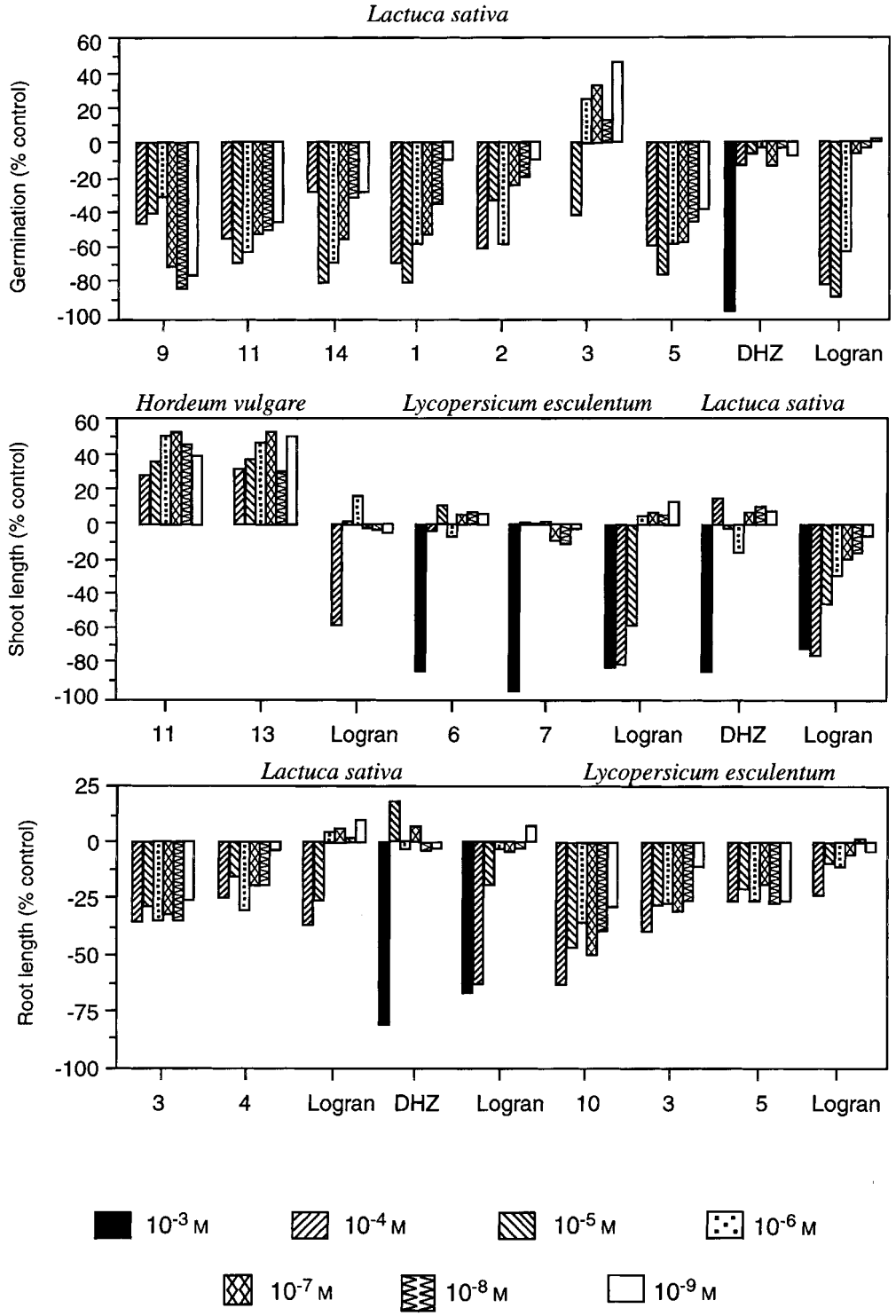

Figure 2. Effect of various compounds on germination root and shoot growth.

development of monocotyledons. This activity was achieved in some cases at doses below those needed for activity with Logran. They can, therefore, serve as template molecules for further studies on potential herbicides.

ACKNOWLEDGEMENTS

This research has been supported by the Secretaría General del Plan Nacional de I+D (CIYCT; AGF97-1230-CO2-02), Spain. We thank FITÓ SA and Novartis for providing seeds and commercial herbicides for bioassays, respectively.

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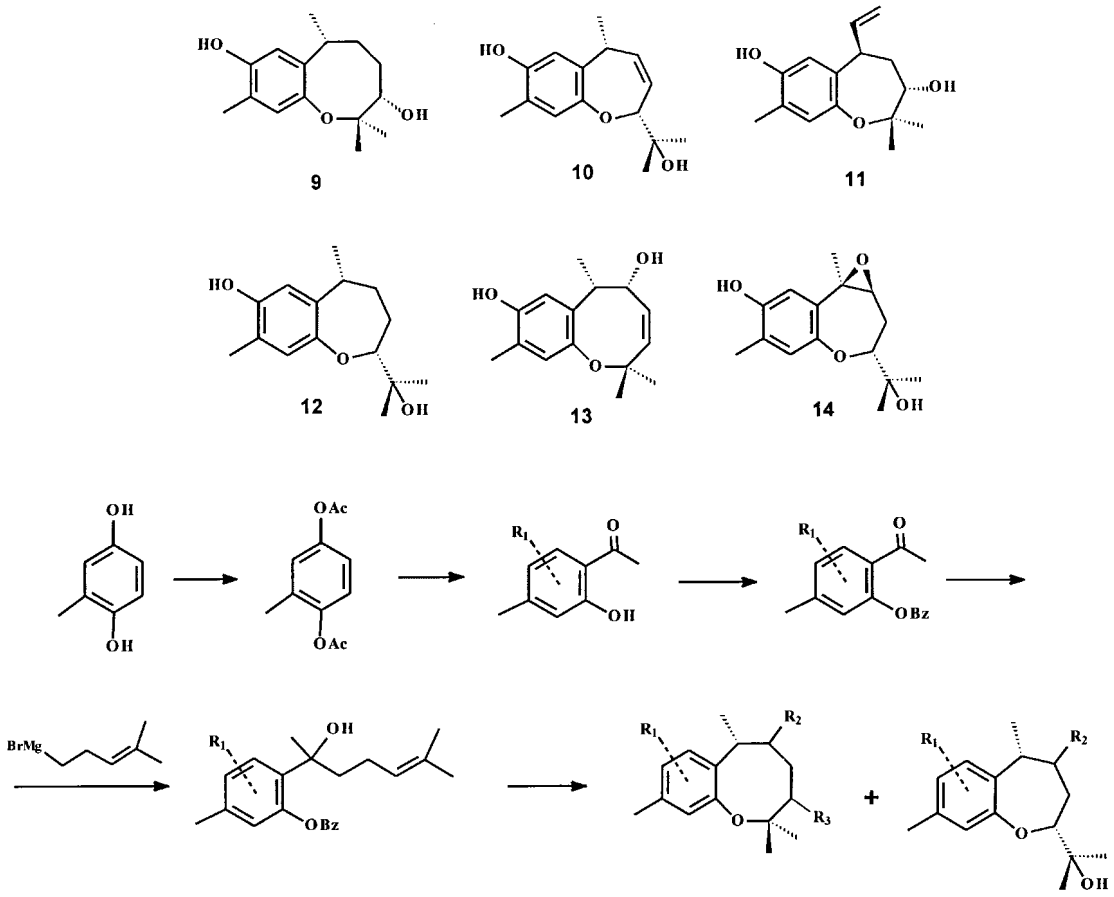

Figure 3. Synthesis routes for heliannuols.

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Interactions of picrodendrins and related terpenoids with ionotropic GABA receptors of mammals and insects

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Abstract: Different structural features govern the interaction of picrodendrins and related terpenoids with rat and with housefly GABA receptors. This supports previous studies which suggest that there are significant differences between the structures of the binding sites in these two receptors.

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(*Received 30 June 1998; accepted 16 February 1999*)