

RELATIONSHIPS BETWEEN THE STRUCTURE OF FLAVONOIDS AND ANTIFEEDANT ACTIVITY AGAINST *MYTHIMNA UNIPUNCTA* (HAWORTH) (LEPIDOPTERA: NOCTUIDAE)

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A group of 30 flavonoids was tested for antifeedant activity against *Mythimna unipuncta* Haw (Lep., Noctuidae) to determine structural characteristics responsible for activity or inactivity of the flavonoids. The presence of a keto group at C4 of the flavonoid was considered to be important for the antifeedant activity. Hydroxylation as well as glycosidation of rings A and B seemed to be important. However, the functional group in the C-ring was not considered to be a significant factor in determining activity of the compound.

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A actividade fagoinibidora de um grupo de 30 flavonoides foi testada relativamente à *Mythimna unipuncta* com o fim de serem determinadas características estruturais responsáveis pela actividade ou inactividade dos flavonoides. A presença de um grupo carbonilo no C-4 dos flavonoides foi considerada importante para a actividade fagoinibidora. A hidroxilação ou a presença de açúcares nos anéis A e B parecem ser factores relevantes. Contudo, o grupo funcional no anel C não é considerado como sendo um factor significativo na actividade apresentada pelo composto.

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INTRODUCTION

Plant flavonoids have been shown to possess activity in a variety of biological systems (NICOLLIER et al. 1981, ZIELSKE et al. 1972, DOSKOTCH 1973, HEDIN et al. 1968, NIELSEN et al. 1979). Flavonoids have been implicated as factors of resistance to insects in several studies (WAISS et al. 1979, CHAN et al. 1978, HEDIN et al. 1983, FEENY 1968, CHAN et al. 1978). A group of 40 flavonoids has been examined for antigrowth activity toward the corn earworm

Heliothis zea Boddie, and discussed with respect to structural features affecting activity (ELLIGER et al. 1980).

Mythimna unipuncta is one of the major pests of pasture lands of Azores (GARCIA & TAVARES 1980).

In this study, we have tested 30 flavonoids for antifeedant activity against *Mythimna unipuncta* to determine whether differences in structural characteristics of the flavonoids (Fig. 1) affect its aptitude for feeding. To establish a rapid screening method to predict compounds having

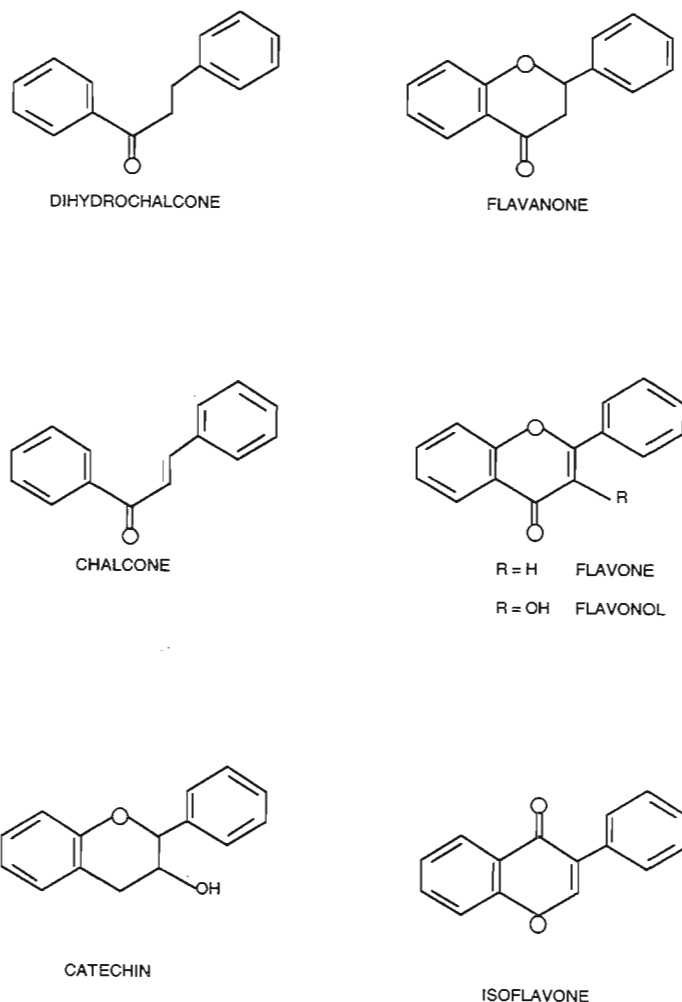


Figure 1 - Skeletal type of some flavonoids (GEISSMAN et al. 1969).

antifeedant activity against *Mithymna unipuncta* was also pretended with this study.

MATERIAL AND METHODS

The flavonoids tested were obtained commercially (Sigma Chemical Company, Extra Synthese and Aldrich Chemical Company) or isolated from a natural source (MILES et al. 1990).

The bioassay procedure developed by Lidert (LIDERT et al. 1985) was used. A test emulsion containing the sample to test (50.000 ppm) was

prepared. Methanol 5% (v/v) Acetone 5% (v/v), Triton CD-7 (surfactant from Rohm & Hass Co.) 0.1%, and distilled water 89.9% (v/v) was used as solvent. Circular leaf discs with 3cm of diameter were punched out of the first true leaves of corn and 35µl of the test emulsion were spread onto their upper surface. The check discs received blank emulsion containing all ingredients with the exception of the test sample.

The treated leaf discs were individually placed if Gelman petri dishes (5cm diameter) containing 4.7cm diameter moist Gelman Filter with 1.5ml of water. After the emulsion was

evaporated to dryness, the leaf discs were infested with third instar test larval insects (one insect/dish). All treatments were replicated five times. The percentage of feeding was determined visually 2,4 and 6 days after treatment.

RESULTS AND DISCUSSION

The results of the bioassay are given in Table 1. At first inspection, there do not appear to be any obvious relationships between flavonoid structures and antifeedant activity; however, if particular structural characteristics are considered, some relationships can be recognized.

The presence of a keto group at C4 seems to be important for the inhibitory activity for feeding as catechin (28) is inactive while quercetin (13) is very active.

With respect to hydroxylation in ring A (Fig. 1) of flavone aglycones it seems that maximal activity is achieved with a 7-hydroxy group in the flavone (3), which is very active, while 3-hydroxyflavone (1) is inactive. It is interesting to note that the farther the hydroxyl group is from the carbonyl group the higher the activity of the compound.

With flavone and flavonol aglycones that have only hydroxyl substituents there is a general trend toward higher activity as the number of hydroxyl groups increases. It has been suggested that the toxicity of flavonoids to *Heliothis zea* Boddie larvae may be linked to solubility or polarity (ELLIGER et al. 1980), which may also be implicated here. However, this cannot be the only consideration as there are even variations among those compounds having the same number of hydroxyl groups.

When considering the effects of glycosidation of flavones and flavanones it can be concluded that in general the glycosides show better activity than the corresponding aglycones (with the exception of myricitrin). However, that increase on activity for glycosides should not be explained solely on the increase of polarity as the position of glycosidation and the type of the sugar also may affect. It can be assumed as conclusion that

there are also interactions with sugar unit. Flavonoids presented antifeedant activity regardless to their class.

Table 1

Antifeedant activity against *Mythimna unipuncta* of 30 flavonoids.

| | Compound | Hydroxylation | Antifeedant activity |
|-------------------------------|--------------------------------------------------------|----------------|----------------------|
| <i>Flavones and flavonols</i> | | | |
| 1 | 3-hydroxyflavone | 3 | N |
| 2 | 6-Methoxyflavone | | + |
| 3 | 7-Hydroxyflavone | 7 | +++ |
| 4 | Chrysin | 5,7 | N |
| 5 | Apigenin | 5,7,4' | N |
| 6 | Cosmetin | 5,4' | N |
| 7 | Acacetin | 5,7 | N |
| 8 | Apiin | 5,4' | N |
| 9 | Fisetin | 3,7,3',4' | N |
| 10 | Luteolin 7-O-glucoside | 5,3',4' | + |
| 11 | Diosmin | 5,3' | N |
| 12 | Tangeritin | 5,6,7,8,4' | + |
| 13 | Quercetin | 3,5,7,3',4' | ++ |
| 14 | Isoquercitrin | 5,7,3',4' | + |
| 15 | Rhamnetin | 3,5,3',4' | + |
| 16 | Rutin | 5,7,3',4' | + |
| 17 | Morin | 3,5,7,2',4' | N |
| 18 | Myricitrin | 3,5,7,3',4',5' | N |
| 19 | Karanjin | 3,5,7,3',4' | ++ |
| 20 | Chrysoeriol | 5,7,4' | ++ |
| <i>Isoflavones</i> | | | |
| 21 | Biochanin | 5,7 | + |
| <i>Flavanones</i> | | | |
| 22 | Naringenin | 5,7,4' | N |
| 23 | Naringin | 5,4' | N |
| 24 | Hesperetin | 5,7,3' | N |
| 25 | Hesperidin | 5,3' | + |
| <i>Chalcones</i> | | | |
| 26 | Chalcone | | ++ |
| 27 | Butein | 3,4,2',4' | ++ |
| <i>Dihydro-chalcones</i> | | | |
| 28 | Phloretin | 4,2',4',6' | N |
| 29 | 3'-Formyl-2',4',6'-trihydroxy-5-methyl dihydrochalcone | 2',4',6' | +++ |
| <i>Catechin</i> | | | |
| 30 | (+)-catechin | 3,5,7,3',4' | N |

+++ Corresponds to 90-100% feeding control;

++ Corresponds to 60-90% feeding control;

Corresponds to 30-60% feeding control.

$$\% \text{ feeding control} = \frac{[1 - (\% \text{ feeding sample})]}{(\% \text{ feeding blank})} \times 100$$

There is enhanced activity of the chalcones as compared to the corresponding flavones, so that coplanarity of the flavones may hinder their biological efficacy. The maximal activity was presented by the dihydrochalcone (30).

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