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M. GÁBOR
F. KÁLLAY

FLAVONOID AND BIOFLAVONOID

PROCEEDINGS OF THE FIFTY SYMPOSIUM

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FLAVONOIDS AND BIOFLAVONOIDS CURRENT RESEARCH TRENDS

PROCEEDINGS OF THE FIFTH HUNGARIAN
BIOFLAVONOID SYMPOSIUM
MÁTRAFÜRED, HUNGARY, MAY 25-27, 1977

Edited by

L. FARKAS

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PREFACE

The 5th Hungarian Bioflavonoid Symposium was held in Mátrafüred, Hungary, from 25th to 27th May, 1977. The meeting was organized by the Work-Committee for Flavonoid Research of the Hungarian Academy of Sciences and the Hungarian Chemical Society.

This symposium, like its predecessors, dealt with all aspects of the chemistry and biochemistry of flavonoid compounds. Participants from ten countries represented most of the major European schools of flavonoid research; recent activities in this field were reported in 43 papers, dealing with new flavonoid structures, results in the synthesis and organic reactions of flavonoids, up-to-date methods of their structure elucidation and instrumental analysis, their absorption and metabolism in plants and in the animal organism, physiological actions, antioxidant properties, and with their dietary and therapeutic value. The contributions contained in this volume thus reflect current interests and trends on all research fronts of these important natural compounds.

It is pointed out that the camera-ready technique has been used in the production of this book in order to ensure rapid publication. Thus editorial work has mostly been limited to the correction of any misprints in the original papers which might otherwise have interfered with the meaning. Illustrations have been reproduced as submitted.

In publishing these papers our intention has been to make them available to all researchers who could not attend the symposium though they share our interest in this field of chemistry and biochemistry.

September 1977
Budapest, Hungary

The Editors

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OPENING ADDRESS

by
PROF. L. FARKAS

Ladies and Gentlemen,

In the preface of his book published in 1962, Professor Geissman wrote: "It is of considerable interest to note that many of the men whose names are among those celebrated in organic chemistry began their scientific investigations in the chemistry of flavonoid substances"

Professor Geissman was stating a fact. It is also a fact that many of those sitting here now have a very good name in organic chemistry; and, beyond doubt, many more of our younger participants will gain such a name. The driving force behind our work is not, however, the possibility of acquiring a celebrated name; the force is our interest in this fascinating realm of pure organic chemical, biochemical and applied research.

This interest is reflected in the number of participants; the number always shows a considerable increase compared with the previous symposium. We are proud that by organizing these symposia we can play our part in the development of flavonoid chemistry, and that by doing so, we can contribute to the improvement of contacts between flavonoid chemists, phytochemists, and biochemists from all over the world.

I open the Fifth Hungarian Bioflavonoid Symposium by extending you a very hearty welcome on behalf of the Hungarian Academy of Sciences, by wishing you a useful time in listening to the lectures, and by hoping that the friendship and cooperation between us will be further promoted by this meeting. In short, I wish you a beneficial time in the pleasant surroundings of Mátrafüred.

Herewith, I declare the Symposium open.

ADDRESS OF WELCOME

by
PROF. P. NÁNÁSI

Ladies and Gentlemen,

On behalf of the Presidium of the Hungarian Chemical Society I welcome the lecturers and all participants of the Symposium from abroad and from Hungary.

It is an endeavour of our Society to assist the organization of international scientific meetings, particularly in those fields where significant results have been achieved by Hungarian scientists. We are aware of the importance of having good contacts with our foreign colleagues working in the same or related fields and of getting acquainted with their results. I am sure that this Symposium belongs to this series.

Although I am not personally involved in this branch of science, it is a great pleasure for me to note that I have been familiar with several of the foreign participants for a long time, as this is not their first trip to Hungary.

I wish successful work to all of you at this meeting; I wish further development of both scientific and personal connections; I wish, moreover, not only useful but also a pleasant pastime during these days of the Symposium.

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FLAVONOIDS OF UNCOMMON STRUCTURES

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Flavonoids, mainly on the basis of the pioneering work of Hungarian scientists from Szent-Györgyi to Gábor, have been shown to be important factors in capillary resistance. Moreover, they have demonstrated important properties as anti-inflammatories and synergists of ascorbic acid.

A large number of biological researches have given a great deal of experimental evidence to these properties, and for this reason a certain number of flavonoids have entered into modern therapy.

We must now consider other biological properties of flavonoids so far neglected. These properties are connected with the function and role of flavonoids in plants, which so far have not found a suitable interpretation.

In recent years flavonol pigments have been considered responsible for ultraviolet absorption in the nectar guide of flowers.

There is at present evidence that flavones act to attract and direct the pollinating insects in flowers. This fact has been demonstrated for Rubbeckia hirta (Compositae), which contains three flavonol glucosides, namely: quercetagenin, patulitrin and 6,7-dimethoxy-3',4',5'-trihydroxyflavone -3-O-glucoside /1/. These substances are present in the petal bases and show an intense spectral absorption at 340-380 nm and are invisible to man but quite visible to insects. These findings suggest that these pigments serve specifically for indicating the nectar guides to insects, not only in this plant but in all plants where flavonoids are present.

Another approach to the understanding of the role of flavonoids in plants may be connected with the utilization of light in the plants. In effect it was observed that the same plant or plants grown at various altitudes show a different flavonoid composition. Although research in this field has not been sufficiently developed, it has been shown that there is

a direct relationship between the altitude and the number of hydroxyl groups present in the flavones of plants.

This fact could be related to the function of flavonoids in the photosynthetic processes and in the absorption and utilization of light in the plant.

Another aspect of the biological function of flavonoids is related to the resistance to diseases of some species of plants. For example, in Coffea arabica it has been shown that resistant varieties contain a higher percentage of quercetin.

Also these studies are only just beginning and may be of considerable interest in establishing the role of flavonoids in plants. They may also indicate a possible mechanism in the resistance of plants to plant diseases.

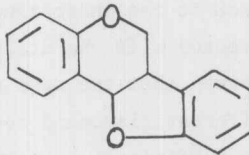
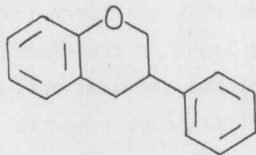
This fact should also be related to the so-called phytoalexins, which are flavonoids formed in Leguminosae when the plant is attacked by a pathogenic fungus. These substances should have the function of enhancing resistance.

Other phytoalexins are also found in other plant families out of Leguminosae but belong to the groups of furans and terpenes.

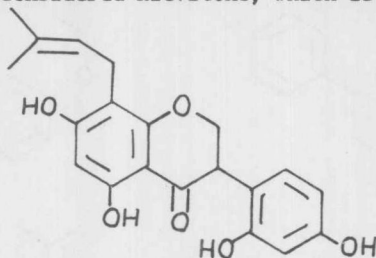
According to Ingham, the flavonoid phytoalexins "are post-infectional metabolites whose formation involves either gene de-repression or activation of a latent enzyme system." Cruickshank considers phytoalexins "fungal-elicited host metabolites with anti-fungal activity, formed in hypersensitive tissues which play a primary role in the inhibition of fungal growth in vitro."/2/

As above reported, phytoalexins belong to three chemical groups: flavonoids including pterocarpan, terpenes and furans. The more important, because of the more intensive research work performed, are the flavonoids, which so far have been found only in Leguminosae.

The flavonoids which display this activity are generally isoflavone derivatives and can be considered derived from two subgroups: the isoflavans and the pterocarpan.



Isoflavans derive from a reduced pyrone ring of the isoflavan; an intermediate product can be considered kievitone, which is a true isoflavanone.



Isoflavan phytoalexins are sativan, vestitol and 2'-methoxy-phaseollin-isoflavan and 2'-methoxy-phaseollidin-isoflavan.

The pterocarpanes are also flavonoids which result from the condensation of the hydroxyl group in 2' of ring B with the hydrogen of an isoflavan system. The more important are: pisatin, of Pisum sativum; medicarpin, of Vicia faba; phaseollin and phaseollidin of Phaseolus vulgaris, which are all considered phytoalexins /3/.

The role in the plant, the function in defending the plant from fungal attack, the mechanism of formation and the possible practical implications of their use in agriculture are at present being examined by various research groups under their chemical and biological aspects.

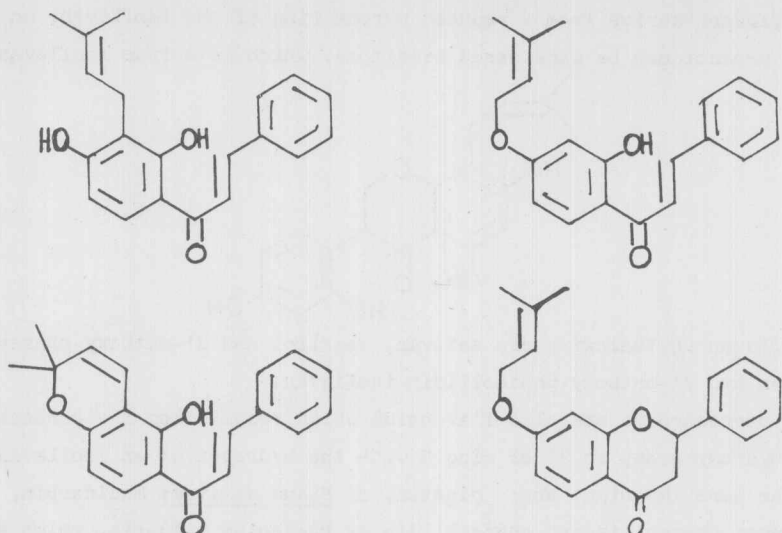
Therefore I believe that the chemist involved in the study of flavonoids should never forget to consider the role of these substances in the plant-microorganism and plant-insect interrelationship, in order to better understand the true role of these substances.

For these reasons, less common or uncommon structures of flavonoids always give rise to new problems and new questions about their role in biological equilibria.

I wish now to consider a number of flavonoids we have recently isolated from several Leguminosae which all show particular structures, probably in relation to some of the disease-resistance mechanism of plants.

If we consider the structures of the flavonoid phytoalexins, we may observe that practically all the substances present an isoprenyl moiety free (kievitone, 2'-methoxy-phaseollin-isoflavan) or cyclized (phaseollin, phaseollidin, etc.).

The presence of isoprenyl residues is quite frequent in Leguminosae, and many examples can be found in chemical literature concerning this fact. I wish only to recall here the study of Lonchocarpus neuroscapha, which led us to isolate nine chalcones and flavanones, all prenylated.



Recently this work performed on the wood bark of L. neuroscapha has been confirmed by us on the seeds of the same plant. These results indicate a rather complicated biogenesis in the plant of the $C_6-C_3-C_6$ system of the chalcone-flavanone with the isoprenyl group /4/.

If we examine now the phenolic substances present in Leguminosae, and in particular in the genus Derris and Lonchocarpus, we may find four main groups which characterize the various species:

- chalcone-flavanone derivatives
- isoflavone derivatives
- coumarin derivatives
- rotenoids.

All these substances, on a speculative basis, may be referred to a common biogenetic pattern, that is $C_6-C_3-C_6$ + an isoprenyl residue /5/.

Also another system, $C_6-C_2-C_6$, the stilbene, has been recently found in Leguminosae, and could be considered related to the C_{15} derivatives, but its study is beyond the scope of the present report.

It is possible that the above groups can be used as taxa in evaluating the classification of many species in the genus Lonchocarpus and Derris. In these species, in effect, we may find all the four groups of substances above reported, more frequently chalcone-flavanones and isoflavone derivatives than coumarins and rotenoids.

At any rate, if we consider the chemical relationship between these four