INSECTICIDAL PROPERTIES AND C CONSTITUTION

Part I. Some Simple Flavone Derivati

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IT is very difficult to give an explanation of the remarka perties of the pyrethrins and of rotenone and its allies in on their chemical constitution. Their molecular structure and further many factors of chemical and physical nature to their success. However, Läuger *et al.*[1] have in their in paper on natural and synthetic insecticides, suggested th the atom grouping (I) and in rotenone the grouping (II) fo There is experimental support for grouping (I) from t coumarin derivatives and of the derivatives of pulvinic aci No data appear to be available from the study of simple s of grouping (II) as toxophore. The simple chromones suggest themselves as suitable compounds for this pu ments of Mahal[2] however seem to indicate that these such action. He used chrysin, genkwanin, 7-hydroxy hydroxyflavone and calycopterin and found that they had and tape worms and leeches. But calycopterin was clai mintic action by earlier workers[3] and karanjin, a flavono to be toxic to fish.[4] There was therefore need for a car the subject.

I

II

Using fresh-water fish (*Haplochilus panchax*) as ex and adopting the criterion of toxicity already described cation[4] from these laboratories, the following series have now been tested for their toxic properties: 7-hyd dihydroxy flavone, galangin, kæmpferol, quercetin and m these hydroxy compounds are found to be feebly tox effect is found in galangin, 3:7-dihydroxy flavone co two are fairly toxic. But there is considerable fall in

on the one hand and kæmpferol and the higher members on the other. The former is found to take over 12 hours to produce the toxic effect in a concentration of 20 mg. per litre. The latter are without any appreciable toxicity. There is difficulty in experimenting with highly hydroxylated compounds owing to their sparing solubility in water.

The methyl ethers of the above compounds as also of some others (methyl ethers of herbacetin, gossypetin and quercetagetin) have been studied. They are more convenient to deal with in virtue of their greater solubility in water. But the remarkable point is that they are considerably more toxic. Obviously the factor of lipoid solubility has been provided in these ethers and these simple flavone derivatives are markedly toxic thus proving beyond doubt that the γ-pyrone ring is a toxophore. From the results given below it is clear that the simplest compound, 7-methoxy-flavone is the most toxic, and the toxicity decreases as the number of methoxy groups in the flavone molecule increases. This ether series therefore differs from the hydroxy compounds which exhibit a maximum of potency in galangin. With these strong fish poisons the curves relating to the concentration and time of toxicity indication (turning time) have the characteristic hyperbolic portions as found in similar cases.[4]

The following table gives the data obtained in one series of experiments. Though variations may arise in the exact turning times due to seasonal and individual variations in the susceptibilities of the fish which are obtained from a big tank, the compounds fall in the same order in different experiments. For the purpose of roughly indicating the degree of toxicity the reading obtained for rotenone under the same conditions is also included.

Name of the compound	Concentration per litre	Turning time
	mg.	minutes
3:7-Dihydroxy flavone ..	20	35·0
Galangin ..	20	15·0
7-methoxy flavone ..	20	2·7
	10	5·0
3:7-dimethoxy flavone ..	20	7·0
	10	19·5
Galangin trimethyl ether ..	20	7·5
Kæmpferol tetramethyl ether ..	20	9·5
Quercetin pentamethyl ether ..	30	35·0
Herbacetin pentamethyl ether ..	30	25·0
Myricetin hexamethyl ether ..	30	37·0
Quercetagetin hexamethyl ether ..	30	33·5
Rotenone ..	1·0	6·5

Though the toxicity decreases with increasing number of methoxyl groups there are a few noteworthy features. There is marked drop from

kæmpferol tetramethyl ether to quercetin pentamethyl ether, but there is not much difference between this pentamethyl ether and the next higher member, myricetin hexamethyl ether. These involve changes in the side phenyl nucleus. A rise from one to two methoxyl groups in this part is accompanied by considerable loss in toxicity, but an increase to three does not mean any further difference. Probably for this reason herbacetin pentamethyl ether is definitely more toxic than its isomer quercetin pentamethyl ether. This point could not be checked further using gossypetin hexamethyl ether due to its sparing solubility in water; comparable and effective concentrations could not be reached. But quercetagetin hexamethyl ether has more or less the same toxicity as its isomer myricetin hexamethyl ether which again, as pointed out earlier, is equal to quercetin methyl ether in this respect.

Summary

The simpler methoxy flavones and some of the corresponding hydroxy compounds are markedly toxic to fish. This definitely establishes that the pyrone ring containing the atom grouping **II** is a toxophore.

References

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4. Krishnaswami and Seshadri .. *Proc. Ind. Acad. Sci.*, (**A**), 1942, **16**, 231.