

endoparasites of fishes, the strigeid trematode, *Cotylurus erraticus*, was reported to form massive metacercarial infestations around the heart of powan, *Coregonus clupeoides*; with an incidence of 100 per cent in Loch Lomond but apparently absent from these fish in Loch Eck, their only other habitat. Present also in trout from Lochs Lomond and Leven, *Cotylurus* does not attain in them the same high infestation. This difference in degree of infestation may be related to differing habits of the hosts, in that trout are fluvial for at least their first year, whereas *Coregonus* spends its whole life in the lake.

The pseudophyllidean cestode, *Trienophorus nodulosus*, occurs in pike in Loch Lomond, and its finding constitutes the second record for Britain. Since plerocercoids of this species have been found only in yearling pike, it would appear that the life-cycle is dependent on cannibalism. Apart from the consideration of their parasites, pike were shown to have a phase in development which is probably the retention of an archaic actinopterygian characteristic. The embryos hatch when the branchial region, pectoral fins and mouth are still imperfectly developed and, for a period of about ten days, hang suspended from water plants. They are attached to the support by the secretion of two cement glands placed in front of the eyes.

An addition to the Scottish fauna was established among the fishes. A biometrical study of char, *Salvelinus alpinus*, recently discovered in Loch Eck, Argyll, yielded results which give this fish the rank of a distinct sub-species.

¹ Ohle, W., *Naturwiss.*, 25, 3 (1937).

² Mortimer, C. H., *J. Ecol.*, 29 (2), 49 (1941).

³ Nygaard, G., *Kon. Danske Videnskabernes Selskab., Biol. Skr.*, 7 (1) 293 (1949).

CHEMISTRY OF OXYGENATED HETEROCYCLIC COMPOUNDS

INTERNATIONAL COLLOQUIUM AT LYONS

LESS than two months after the Dublin symposium on naturally occurring pyrones (see *Nature*, 176, 637; 1955), a similar meeting devoted more particularly to naturally occurring flavonoid compounds, was held in Lyons during September 5-10. Twenty-six scientists from ten different countries took part in these discussions, during which the different aspects of the chemistry of oxygenated heterocyclics were reviewed.

The first series of reports were in the field of organic chemistry. M. Mousseron (Montpellier) discussed the reactions of epoxides in relation to their steric structure. He suggested a new method for their quantitative estimation in the presence of $-SCN$ ions. The fixation of water by epoxy-1:2-cycloalkanes was discussed. The epoxide structure occurs in the transition states of many reactions and leads to compounds having a *trans* configuration.

G. Sandris and G. Ourisson (Paris) discussed the synthesis and properties of 2:2:5:5-tetramethyl-tetrahydrofuran. Mention was made of the effect, on the spectral properties of this type of compound, of replacement of the heterocyclic oxygen by methylene. In some cases, for example, when there was an α -diketonic group in the 3- or 4-position, the authors achieved a molecular rearrangement to a four-membered ring (trimethylene oxide).

The chemistry of coumarins in general was reviewed by N. P. Buu-Hoi (Paris). The most reactive position in coumarone is the 2-position, while in thionaphthene it is at the 3-carbon. A molecule like brasane is far less reactive than the analogous polycyclic hydrocarbon (naphthacene).

C. Mentzer (Lyons) gave an account of the synthetic methods leading to benzopyrone compounds (coumarins, chromones, flavones and their derivatives). The methods were classified according to linkages formed. The condensation of an aromatic C_6 group with C_3 molecules was discussed in detail. A complete list of coumarins, chromones and flavanones, obtained by the author and his collaborators by the 'thermal condensation' of phenols with malonic or β -ketonic esters, was given.

A. Dreiding (Zurich) has synthesized 5:6:7:8-tetrahydrocoumarin by a Reformatsky reaction between ethyl monobromacetate and 2-(hydroxymethylene)-cyclohexanone. It may be possible to apply this method to the synthesis of other α -pyrones starting from β -dicarbonyl derivatives.

In a second series of papers, the oxygenated heterocyclics were discussed with emphasis on the biochemical aspects. As in the Dublin symposium, the flavones and their derivatives, as well as other less well-known lactones, were the focus of attention.

T. R. Seshadri (Delhi) showed the possibility of the *in vitro* transformation of flavanones into dihydroflavonols by the addition of an oxygen atom to the 3-position. This can be achieved: (a) by bromination or iodination of the acetyl derivative of the flavanone and subsequent treatment with silver acetate; (b) by the action of lead tetra-acetate; (c) by the action of Fenton's reagent (hydrogen peroxide + ferrous ion) on the acetyl derivatives.

T. S. Wheeler and E. M. Philbin (Dublin) discussed molecular rearrangements in the flavonoid field. The Wessely-Moser rearrangement has been extended to chromanols and dihydroxyxanthenes. A new type of rearrangement was described in which the 2-aryl nucleus takes the place of the second benzene nucleus in the flavone molecule.

The chemistry of natural aurones was reviewed by T. A. Geissman (Los Angeles). These substances (benzal-2-coumaranones) occur in many higher plants of the genera *Cosmos*, *Coreopsis*, etc. The author, who recalled the work of Marini-Bettolo, Hattori and others, has studied their synthesis, properties, detection in plants, isolation and spectral properties in relation to structure.

S. Hattori and M. Shimokoriyama (Tokyo) presented two reports, one dealing with flavonic glycosides from the leaves of *Calystegia japonica* and *hederacea*, the other on the localization of the flavonoid pigments in '*Cosmos sulphureus*'. It is interesting to note that *Calystegia japonica* Choisy (Convolvulaceae) contains a rhamnoglucoside of kempferol, in which the disaccharide unit located in position 3 has been identified as rutinose, while *Calystegia hederacea*, a species so similar as to be easily mistaken for the former, contains kempferol 3-galactoside identical with trifolin from the flowers of *Trifolium repens*.

Dihydroflavonols were discussed by J. Gripenberg (Helsinki). These compounds are of interest because of the manner in which they become rearranged in alkaline media. In contrast to what happens in aurones, the rearrangements of dihydroflavonols are accompanied by contraction of the heterocyclic ring.

T. Swain (Cambridge), in the course of investigations on the chemical composition of some horticultural varieties of *Dahlia variabilis*, has found that the petals and leaves of some of these plants contain aglycones, which have not hitherto been discovered in this species, namely, sulphuretin, 2':4:4'-trihydroxychalkone, naringenin, eriodictyol, quercetin and kempferol.

H. Erdtman (Stockholm) outlined the comparative biochemistry of the genus *Pinus*. The following flavonoid constituents have been identified in extracts of the heartwoods of these species: chrysin, tectochrysin, 6-methylchrysin, 2:3-dihydrochrysin, 2:3-dihydrotectochrysin, pinobanksin, pinobanksin 7-methyl ether, strobopinin, cryptostrobin, and strobobanksin. Here the distribution of these substances shows a positive taxonomic interest. Botanists divide the genus *Pinus* into two parts, namely, diploxylon and haploxylon. In the diploxylon species, no flavones are encountered, only flavanones occur; in the haploxylon species, however, flavones and flavanones exist simultaneously.

F. E. King (Nottingham) has isolated derivatives of the catechin group (3-hydroxyflavans) in the heartwoods of many species of *Azalia*. He re-examined classical views concerning the structure of such derivatives and, in the light of present stereochemical theory, he concludes that the 'epi' series should have a 'cis' configuration. Melacacidin, another component isolated from the wood of *Acacia melanoxylon*, has been identified as 7:8:3':4'-tetrahydroxyflavan-3:4-diol and must be considered as a typical leucoanthocyanidin.

H. Schmid (Zurich) dealt with the chemistry of non-benzopyronic lactones. He described their chemistry and physical properties in relation to molecular structure. Various methods of determining the nature of the heterocyclic ring (pentagonal or hexagonal), the number and positions of the double bonds, etc., were given. He reviewed some naturally occurring well-defined types, for example, protoanemonin, kawain, nepetalactone, etc.

W. Whalley (Liverpool) spoke about sclerotiorin and rotiorin, which are pigments obtained from several strains of *Penicillium sclerotiorum*. They have the empirical formulae $C_{21}H_{22}O_5Cl$ and $C_{21}H_{22}O_6$, respectively, and both contain the same branched C_9 ethylenic chain. They almost certainly possess an α -pyrone ring characterized by the fact that the heterocyclic oxygen can be replaced by $-NH-$ with subsequent formation of the corresponding α -pyridone.

The structure of calophyllolide, a compound isolated from the nuts of *Calophyllum inophyllum*, was discussed by Mme. Polonsky (Paris). This has the empirical formula $C_{28}H_{22}O_6 \pm CH_2$. It is an $\alpha\beta$ -unsaturated- γ -enol-lactone having one methoxyl group. With 40 per cent potassium hydroxide it gives 5-hydroxy-7-methoxy-4-phenylcoumarin ($C_{16}H_{12}O_4$), the structure of which was confirmed by comparison with an authentic sample.

A third series of reports were devoted to analytical work.

Mme. G. Aulin-Erdtman (Stockholm) described the $\Delta\epsilon$ method and its possible application to the analysis of flavone and flavone derivatives. This method is based on the modification of the ultra-violet spectra caused by ionization or other convenient chemical reactions. The change in ϵ -values determined at various wave-lengths (λ) is represented graphically, giving a $\Delta\epsilon$ curve. This curve is a

characteristic of the chromophore, which can be modified and is independent of non-reactive chromophores. The method is sometimes better than ordinary ultra-violet examination in analysing complex natural extracts.

Finally, two papers dealing with the biological properties of oxygenated heterocyclics were presented.

F. Teyeau (Bordeaux) has shown that leucocyanidol, isolated from the teguments of the arachid nut, increases vascular resistance both in animals and in men. Moreover, it possesses anti-anaphylactic properties which might be explained by its inhibitory power towards hyaluronidase. It is fixed by seric proteins, more particularly by the globulin fraction. At a certain concentration it induces formation in serum of a precipitate containing all the lipids and only very small quantities of proteins.

H. Ferrando and J. Bost (Lyons) have studied the action *in situ* of several flavones on the intestines of rabbits. Ferguson has already shown that tricrin (5:7:4'-trihydroxy-3:5-dimethoxyflavone) strongly inhibits contraction of this organ. Its 4'-methoxy derivative, on the contrary, reduces the effects of tricrin.

It will be seen from the summaries that much current work in the field of oxygenated heterocyclics was presented at this colloquium. It is to be regretted, however, that a number of centres of research in the United States, Australia, Africa and Asia could not, owing to geographical considerations, send representatives to the colloquium.

ANIMAL SOUNDS IN THE SEA

DURING the Second World War the ocean waters were widely explored for the first time with sensitive listening devices. Submarine eavesdroppers heard sounds which they took to be from ships where there were no ships, and many mysterious 'beeps', 'groans', 'croaks', 'crackles', 'whistles' and 'moans' came to their earphones. It was suspected that these noises were the chatter of underwater animals, and, after the War, the U.S. Office of Naval Research launched a comprehensive study of sea-animal sounds. This study has been reported by Marie Poland Fish (*Sci. Amer.*, April 1956).

Scientific workers have listened with hydrophones and recorded on tape the sounds of hundreds of species of animals, from shrimps to porpoises. The articulate denizens of the sea 'speak' a confusing variety of dialects, but each is distinctive, and with experience it is possible to identify the kind of animal by its sounds, as one recognizes a familiar voice on the telephone. Listening to tropical fishes in the waters of the Caribbean, trained recorders can recognize them on approach before they come into view. Fishes and other sea animals have no vocal organs: they make sounds in diverse and intriguing ways which sometimes involve a large part of the anatomy.

One group produces sound by vibrating the walls of their balloon-like air bladder, the bladder acting like a sound-box or drum. The toadfish, for example, sets up vibrations of its bladder by means of muscle contractions, and the sound emitted ranges from a grunt to a 'fog-horn' boom. Experiments have shown that the sound originates in the air bladder. When the bladder was removed, the fish could produce no sound. But the air bladder alone, placed