MEETINGS

PLANT TERPENOIDS

A SYMPOSIUM on "Terpenoids in Plants" was held in conjunction with the annual general meeting of the Phytochemical Group at the Department of Agricultural Biochemistry, Aberystwyth, during April 12–14, 1966, under the chairmanship of Professor E. Lederer (Gif-sur-Yvette). The symposium covered aspects of the occurrence, chemical structure, biosynthesis, and biological function of the major groups of terpenoids.

In the opening lecture Professor T. W. Goodwin (University College of Wales, Aberystwyth) reviewed some possible biological functions of terpenoids in plants, in particular the role of abscisin in the control of leaf abscission, the control of carotenogenesis in the (—) strain of *Blakesleea trispora* by trisporic acid and the stimulatory effects of sterols on oospore production by *Phytophthora* spp. and by *Pythium* spp.

The biogenetic isoprene rule was reviewed by Professor D. Arigoni (Federal Technical College, Zurich). In the past few years a variety of sesqui-, di-, and triterpenes have been found which have structures which were not expected from the biogenetic rule. These apparent anomalies, however, can now be explained by several types of intramolecular arrangements which were outlined. Recent work on conformational analysis of terpenoids and steroids was described by Dr. J. S. E. Holker (University of Liverpool). He also showed how the behaviour of terpenoid molecules during chemical reactions was correlated with differences in their molecular geometry.

Methods of synthesis of mevalonic acid labelled with carbon-14 or tritium, or deuterium in specific positions were described by Dr. G. Ryback (Shell Research, Sittingbourne); these compounds can be used in the elucidation of the biochemical mechanisms involved in the biosynthetic conversion of mevalonate to terpenoids. The biosynthesis and metabolism of monoterpenoids was described by Dr. W. D. Loomis (University of Oregon). From the results of experiments in which the incorporation of mevalonic acid and $^{14}CO_2$ into monoterpenes was compared, it was suggested that mevalonic acid was formed near the site of monoterpene synthesis, presumably from sugars. The monoterpenes seem to be metabolically interconverted and these reactions are influenced by illumination and by night temperature.

Dr. A. C. Oehschlager (University of Strasbourg) described *in vitro* transformations, and particularly acid-catalysed stereospecific cyclizations of diterpenes; in many of the transformations the sequence of arrangements follows that of the proposed biogenetic pathways, such as in the acid-catalysed stereospecific cyclization of all-*trans* isoprenoid alcohols to *trans* decalins and the conversion of pimaladiene to abietadiene.

The chemistry of sesquiterpenes was outlined by Dr. M. O. Sutherland (University of Brisbane). Although the sesquiterpenes are derived from farnesyl pyrophosphate, the reactions involved in the further transformations are not clear. For example, the hydrocarbon geijerene which has two asymmetric centres is isolated in racemic form and, therefore, cannot be derived as an artefact of isolation from elemol. The toxic principles of *Myoporum deserti* contain sesquiterpene furanoid ketones, related to myoporone, which seem to arise by extensive allylic oxidation of unsaturated precursors.

The chemistry of triterpenes was reviewed by Dr. T. G. Halsall (University of Oxford). Recent structural determinations on more complex molecules and also on small amounts of compounds have clarified views on triterpene biogenesis. It is now clear that, after the methyl and hydrogen shifts accompanying the initial biosynthetic cyclization of squalene, oxidation occurs which leads not only to ketones and acids, for example, but also to loss of carbon, to bond fission, to further carbon–carbon bond rearrangement and even to new carbon–carbon bond formation. Such reactions were illustrated by reference to a number of triterpenes including platanic acid, nycthanic acid, limonin, swietenine, ecanothic acid and related compounds.

The biosynthesis of phytosterols, reviewed by Dr. L. J. Goad (University College, Aberystwyth), appears to be similar in many respects to that of cholesterol in animals. The extra C_{24}-alkyl groups arise by transmethylation probably shortly after the cyclization of squalene. In plants it seems that lanosterol is not in the biosynthetic sequence but that its place is taken by *cyclo*-artenol which has recently been found always accompanying the plant sterols.

Professor R. Tschesche (University of Bonn) described recent experiments on the biosynthesis of steroid sapogenins and related compounds. 21-^{14}C-Δ5-pregnene-3β-ol-20-one glucoside is converted, in leaves of *Digitalis lanata*, to radioactive digitoxigenin, digoxigenin and gitoxigenin. Similarly, 4-^{14}C-cholesterol glucoside is converted to tigogenin, gitogenin and diosgenin. There must, therefore, be a hydrogenase which saturates the Δ5 double bond to give a *cis* configuration in ring *A/B* and hydroxylases which can introduce hydroxyl groups at C_{11} and C_{16} of digitoxigenin and C_2 of tigogenin.

The introduction of infra-red, nuclear magnetic resonance and precision mass spectrometry into structural studies of carotenoids was described by Professor B. C. L. Weedon (Queen Mary College, University of London). Even if the older degradative methods have to be used they can now be combined with chromatographic analysis of the products so that as little as 5 or 10 mg of carotenoid can be used. The newer methods were used to determine the structures of capsanthin and capsorubin, and also more recently the structures of fucoxanthin and foliaxanthin, both of which are shown to possess allene groupings, have been investigated.

Dr. J. F. Pennock (University of Liverpool) reviewed the chemistry and occurrence of the four major groups of terpenoid quinones, namely the vitamins K, plastoquinones, ubiquinones, and tocopherol quinones. These are all associated with intracellular organelles and their functions are associated with hydrogen transport by conversion to the corresponding hydroquinones although the possibility of biological reactions involved in cyclization to the chromanol forms may also be important.

The biosynthesis of the terpenoid quinones was reviewed by Dr. D. R. Threlfall (Aberystwyth). The three major distal precursors of the quinones appear to be mevalonic acid which gives the terpenoid side-chain, shikimic acid which gives the aromatic nucleus of the *p*-benzoquinones, and methionine giving the ring methyls and methoxyls. Permeability barriers across organelles has hampered many of the biosynthetic studies. It is not yet clear whether prenyl phenols, analogous to 2-decaprenyl phenol, are universal precursors of the terpenoid quinones.

Dr. F. W. Hemming (University of Liverpool) described the recent isolation from green leaves of long chain polyisoprenoid alcohols with chain lengths up to 110 carbon atoms. Each of these so-called prenols has more *cis* than *trans* isoprene residues and some of them resemble the pig liver dolichols because the double bond normally β— to the hydroxyl group is saturated. The *cis–trans* prenols occur as a mixture of isoprenologues, varying with the species, the concentration in green leaves increases with age and the bulk of them is associated with the osmiophilic globules of the chloroplast; the rest occurs outside the chloroplast.

J. FRIEND