Structure and Interrelationship of Orientin and Homo-orientin

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Since the first reported occurrence of orientin and homo-orientin in plant material, it has been recognized that these compounds possess a luteolin (3',4',5,7-tetrahydroxyflavone) nucleus. However, the identity of the aliphatic portions of the molecules and the interrelationship of the two compounds have been a matter of speculation and uncertainty. The structures and interconvertibility of the compounds can, however, now be satisfactorily explained in the light of the following findings.

Oxidation of orientin and homo-orientin tetramethyl ethers with aqueous ferric chloride under conditions previously described and examination of the reaction mixtures for the presence of sugars has yielded the same result for both compounds and in each case analysis has revealed the presence of two sugars, arabinose and glucose, identical with authentic arabinose and glucose respectively by chromatography in benzene—butan-1-ol—pyridine—water 1:5:3:5, by vol., in butan-1-ol—acetic acid—water 20:5:11, by vol. and in 75% aqueous phenol. The presence of a pentose and a hexose in each case indicates that oxidative fission of the aliphatic residue occurs not only between C(1) and C(2) of the glycosyl residue as in the case of barbaloin but also between C(1) of the glycosyl residue and the point of attachment of this residue to the flavone nucleus. The previously reported results for the C-glycoside barbaloin were confirmed in this laboratory with authentic barbaloin, m.p. 146—148°, isolated from commercial aloe, when only traces of glucose could be detected.

Treatment of the periodate-oxidized, borohydride-reduced tetramethyl ethers of orientin and homo-orientin by refluxing in N-aqueous hydrochloric acid for 15 min. resulted, in each case, in the liberation of glycerol. A similar result was obtained by Hänsel and Rimpler for homo-orientin isolated from Vitis agnus castus. Contrary to the findings of Hay and Haynes, glycerol was also obtained from periodate-oxidized, borohydride-reduced barbaloin under the above conditions.

The above findings, together with the results of previous work, indicate that orientin and homo-orientin, like barbaloin, possess C-glycopyranosyl residues.

The interconvertibility of these two compounds is now satisfactorily explained in terms of a ring isomeric change in the flavone portion of their molecules. The following evidence lends support to this theory:

1. Treatment of orientin and homo-orientin tetramethyl ethers under aqueous acid conditions (refluxing in 2 N-aqueous hydrochloric acid for 1 hr.) which caused a partial interconversion of orientin and homo-orientin, failed to cause any interconversion of the tetramethyl ethers. Under the same conditions, 3,4',7-tri-O-methylorientin and 3,4',7-tri-O-methylhomo-orientin underwent a partial interconversion. This is in accordance with the proposed theory which requires the existence of a free 5-hydroxyl group for ring isomerization to take place.

2. Periodic acid oxidation of tetra-O-methylorientin under the conditions previously described, results in the formation of a product possessing a tetra-O-methyl-luteolin nucleus which differs in chromatographic behaviour from the product of periodic acid oxidation of tetra-O-methylhomo-orientin (Rf values 0.76 and 0.90 respectively in butan-1-ol—acetic acid—water 20:5:11, by vol.).

3. The nuclear magnetic resonance spectra of orientin and homo-orientin octa-acetates reveal differences in the pattern of the benzenoid protons of the two compounds. These chemical shifts would be expected were one compound substituted in the 6- and the other in the 8-position owing to unequal shielding of the protons by the acetylated C-glucopyranosyl groups.

It is tentatively suggested that orientin is the 8-substituted luteolin C-glycoside whereas homo-orientin is substituted in the 6-position. This is indicated by the solubility and chromatographic properties of the two compounds, homo-orientin corresponding to saponaretin and orientin to vinitex, this last-named compound having already been shown to be an 8-C-glycosyllflavone.

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4 B. H. Koeppen, Chem. and Ind. 1962, 2145.

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