NUCLEAR REDUCTION OF ANTHOXANTHINS IN THE SIDE PHENYL NUCLEUS

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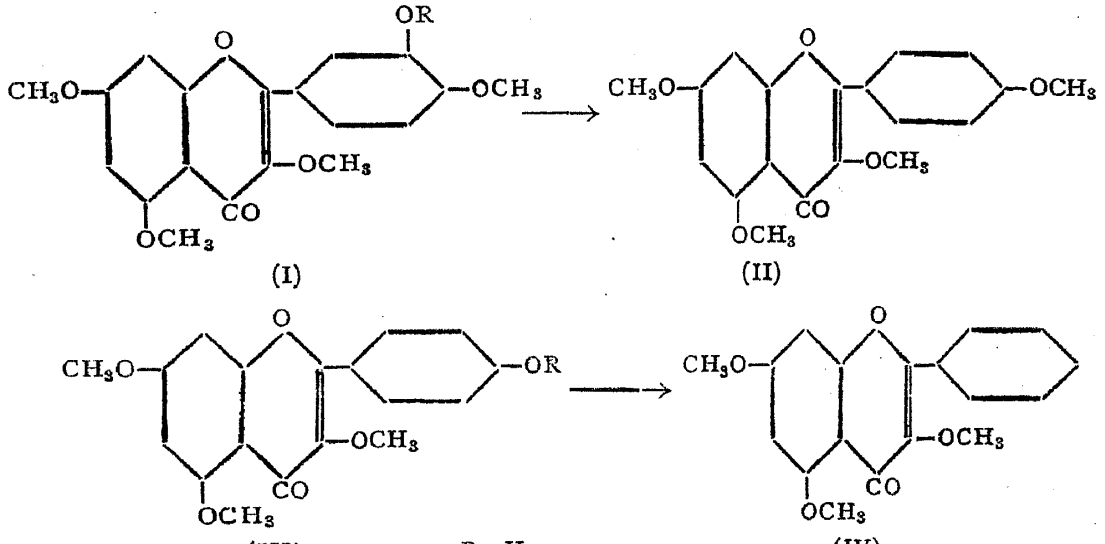
ONE of the implications of the theory of Robinson[1] relating to the biogenesis of anthocyanins and anthoxanthins was that members having the catechol unit in the side phenyl nucleus should represent the earliest stage. Support for this was provided by Lawrence, Price, Robinson and Robinson[2] from a detailed examination of the occurrence of anthocyanins. The data led to the conclusion that cyanidin is the primary member of the anthocyanidin group and the production of delphinidin (oxidation) and pelargonidin (reduction) involve one more stage in the evolution.

In view of the close relationship between anthocyanins and anthoxanthins, the above considerations should apply to the latter also. But here, the process of reduction should be considered to proceed further yielding compounds with no hydroxyl group in the side phenyl nucleus. These stages of reduction have not so far been carried out in the laboratory. As model experiments the nuclear reduction of O-tetramethylquercetin (I *a*) with a free hydroxyl group in the 3′-position has now been successfully done by the hydrogenolysis[3] of its tosyl ester (I *b*). The product is identical with



O-tetramethyl kæmpherol (II). Similarly the trimethyl ether of kæmpherol (III *a*) with a free hydroxyl group in the 4′-position has been converted into galangin trimethyl ether (IV). These results would indicate the possibility of nuclear reduction in the side phenyl nucleus of the flavonoids taking place in nature as mentioned above.

EXPERIMENTAL

3′-Tosyl quercetin tetramethyl ether and 4′-tosyl kæmpherol trimethyl ether

A dry acetone solution of quercetin tetramethyl ether[4] (I *a*) or kæmpherol trimethyl ether[5] (III *a*) (1 mole) was refluxed with tosyl chloride (1·1 mole) and anhydrous potassium carbonate (excess) for 3 hours. Acetone was distilled off and the potassium salts were dissolved in water when a crystalline solid separated out. It was filtered, washed with 5% aqueous sodium carbonate and then with water and dried. 3′-Tosyl quercetin tetramethyl ether (I *b*) crystallised from ethyl acetate-petroleum ether mixture as colourless rectangular rods and prismatic needles melting at 120–22° (Found: C, 59·9; H, 5·0. $C_{26}H_{24}O_9S$, $\frac{1}{2}$ H_2O requires C, 59·9; H, 4·8%). 4′-Tosyl kæmpherol trimethyl ether (III *b*) separated as colourless small rhombohedral plates melting at 280–81° after two crystallisations from alcohol (Found: C, 62·6; H, 5·3. $C_{25}H_{22}O_8S$ requires C, 62·3; H, 4·6%).

Reduction

Each of the above tosyl esters (1 g.) was dissolved in alcohol and Raney nickel (2 tea-spoonful) was suspended in the solution. A slow current of purified hydrogen gas was passed into this well-agitated suspension kept at room temperature (28° C.) for an hour. The mixture was filtered and the alcoholic solution concentrated. The nickel residue was treated with dilute hydrochloric acid, the product extracted with ether and the ether concentrate was mixed with the above alcoholic concentrate. The combined product was refluxed with 5% aqueous sodium carbonate (100 c.c.) for 2 hours and after cooling was extracted well with ether. The ether solution was concentrated when a colourless semi-solid mass separated. It was dried in a vacuum desiccator and crystallised from ethyl acetate-petroleum ether mixture. Yield, 0·1 g.

The 3′-tosyl quercetin tetramethyl ether (I *b*) yielded kæmpherol tetramethyl ether[6] (II) as colourless needles melting at 165–66° alone or when mixed with an authentic sample; while 4′-tosyl kæmpherol trimethyl ether (III *b*) gave galangin trimethyl ether[7] (IV) as colourless needles melting at 195–96° which was undepressed by admixture with a synthetic sample.

SUMMARY

By the application of nuclear reduction a quercetin derivative has been converted into kæmpherol and a kæmpherol derivative into galangin.

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