NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXII. A Synthesis of Pectolinarigenin

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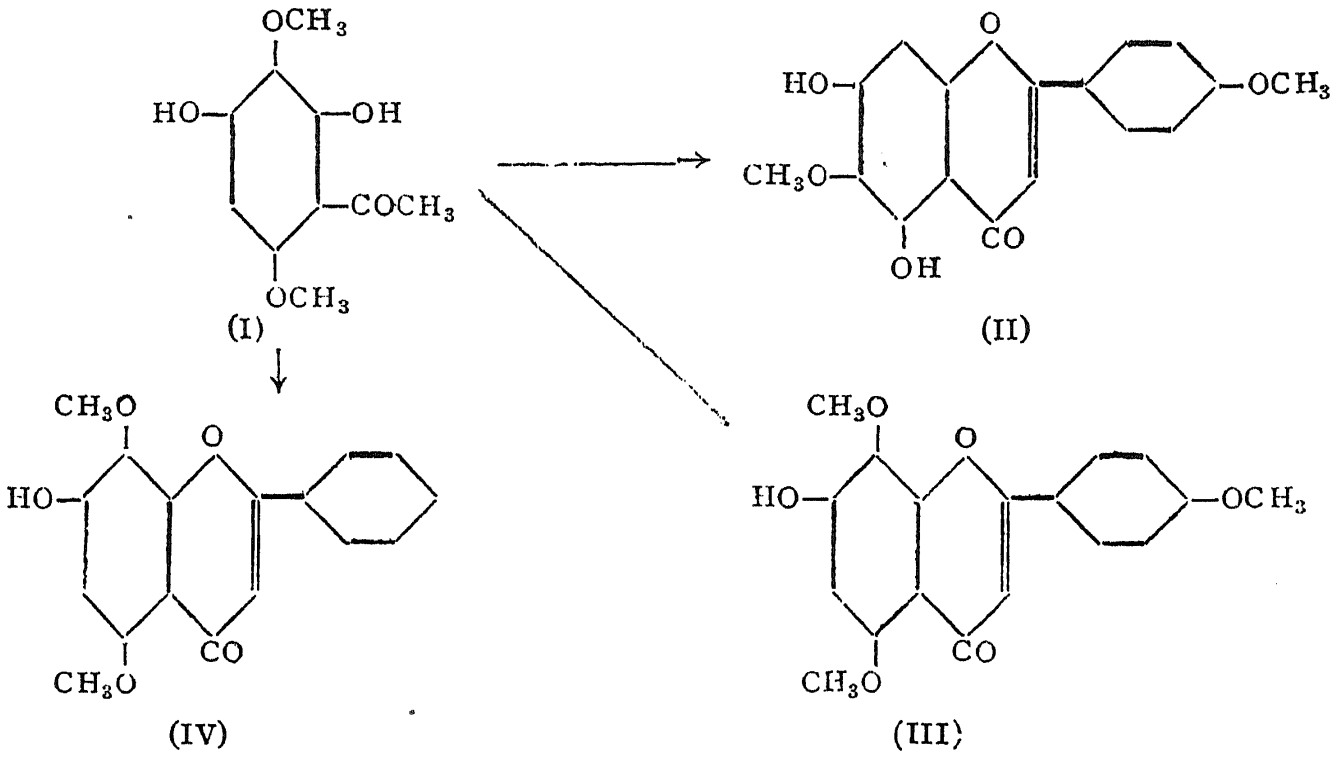
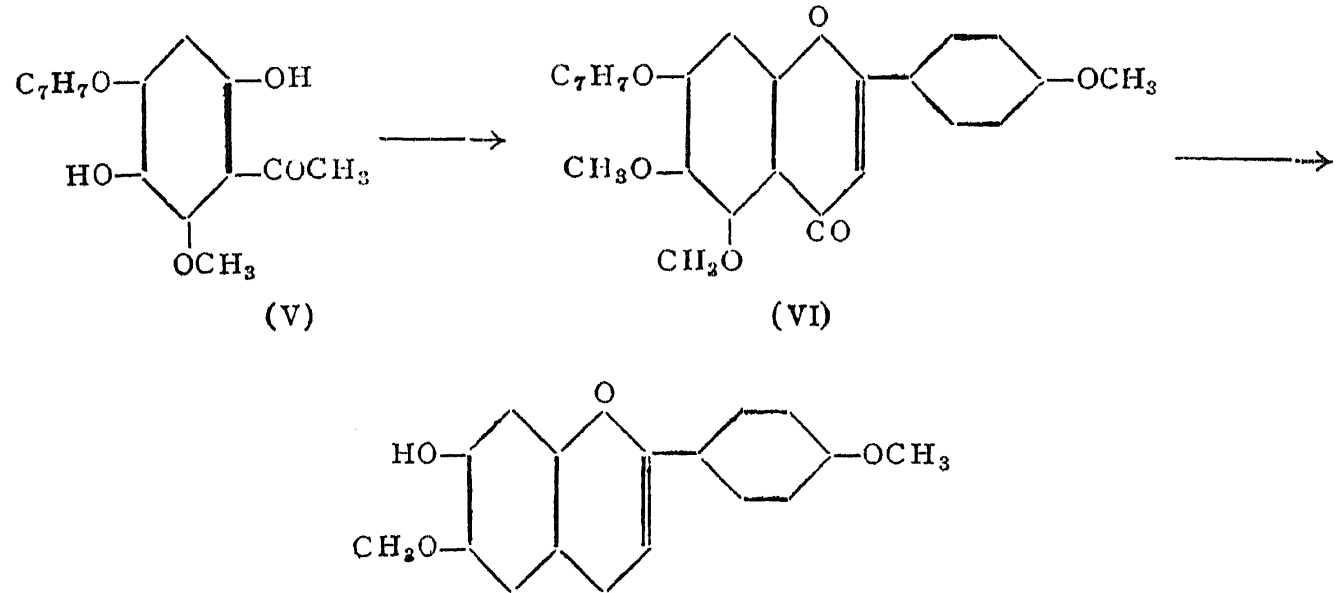
The glycoside pectolinarin which was isolated from the flowers of *Linaria vulgaris*[1] yielded on hydrolysis an aglycone, pectolinarigenin, having the molecular formula $C_{17}H_{14}O_6$. It was a dimethyl ether of scutellarein. The position of one of the methoxyl groups could be easily located since it yielded anisic acid by alkali fission. The other methoxyl was considered to be in the 6-position since the compound was found to be identical with the 6 : 4′-dimethyl ether of scutellarein (II) obtained synthetically by Wessely and Moser.[2] The sugar residue could be allotted the position 7 because the glycoside was unchanged when treated with diazomethane and hence had the free hydroxyl group in the resistant 5-position. Subsequently the synthesis of the glycoside itself has been effected using the aglycone and hexa-acetyl-β-rutinosidyl bromide.[3]

The synthesis of pectolinarigenin by Wessely and Moser[2] was not a direct one and was due to the Allan-Robinson condensation taking an unexpected course. They fused 2 : 4-dihydroxy-3 : 6-dimethoxy acetophenone (I) with anisic anhydride and sodium anisate and instead of the expected 7-hydroxy-5 : 8 : 4′-trimethoxy flavone (III), obtained a dimethyl ether of scutellarein (II). This was explained as due to partial demethylation during the condensation and favoured ring closure to yield the 5 : 6 : 7-arrangement instead of the 5 : 7 : 8-arrangement of groups.

However, attempts to synthesise oroxylin-A by employing the same ketone and benzoic anhydride and sodium benzoate were unsuccessful.[4] Only wogonin methyl ether (IV) was obtained. Even in anisoylation Wessely and Moser got the normal product (III) in one of a large number of experiments and Furukawa and Tamaki[5] reported that the condensation proceeded normally in their experiments to yield 5 : 8 : 4′-trimethoxy-7-hydroxy flavone (III). Hence a more definite synthetic route for scutellarein -6 : 4′-dimethyl-ether was needed and this has now been provided by the synthesis of the



compound on the same lines as oroxylin-A.[6] By fusing 2: 5-dihydroxy-4-benzyloxy-6-methoxy acetophenone (V) with sodium anisate and anisic anhydride and methylating the product, is obtained 5: 6: 4′-trimethoxy-7-benzyloxy flavone (VI). It undergoes debenzylation and partial demethylation in the 5-position with hydrobromic acid and the product is a dimethyl ether having all the properties of pectolinarigenin (II). Its diacetate also agrees with the description of pectolinarigenin diacetate. We have also repeated the synthesis by the method of Wessely and Moser[2] and find that the product is identical with the one obtained by the new method, the same being the case with the diacetate obtained from it.



DIELECTRIC CONSTANTS OF CRYSTALS—III

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1. Introduction

There are discrepancies in the dielectric constants of some crystals in different directions reported by previous investigators. An accurate knowledge of the directional dependence of dielectric constant is required for an understanding of the relation between dielectric behaviour and crystal structure. So the author has undertaken a determination of the dielectric constants of a number of crystals and the results in some of them are reported in this paper.

2. Experimental

Barium nitrate, Lead nitrate and Sodium chlorate.—Plates are cut from transparent, solution grown crystals of the above. As these are cubic crystals, any orientation will give the same constant and so, the plane which gives the largest area is chosen for cutting.

Rocksalt and Fluorite.—Sections are cut from clear transparent minerals. Another two sections of fluorite, one from a green-coloured crystal and one from a pale-blue coloured crystal are also cut.

Spinel.—A plate is taken for investigation from a perfectly transparent, artificially grown lump.

Calcite, Apatite and Citrine.—Sections from flawless, transparent varieties of calcite, apatite and citrine, parallel and perpendicular to the optic axis of each, are cut. Citrine is light yellow in colour.

Zircon.—An opaque brownish crystal with well-developed faces is used for taking sections.

Beryl.—Specimen I is colourless and specimen II is of green colour. These are not quite transparent, but somewhat cloudy.

Corundum.—Three different specimens are used. All are opaque. Specimen I is chocolate coloured, specimen II is of brown colour with uniform

texture and specimen III is of slate colour with specks of foreign material embedded here and there.

Tourmaline.—Different specimens are used. Specimen I is translucent and light yellow in colour. Some portion of it is green. Specimen 2 is rose red in colour, and transparent. In thin sections, it is almost colourless. Specimen 3 is black in bulk, but dark green and transparent in very thin sections. Specimens 4, 5, 6, 7, 8, are all black in colour. All the crystals have well-developed faces.

Sulphur and Barites.—These are orthorhombic crystals and sections $\perp^r$ to the three crystallographic axes *a*, *b*, *c* are required. The three sections are obtained from three small, solution grown crystals of sulphur, which are clear and transparent. Barites, used for taking the sections, is a perfectly transparent and colourless mineral.

The dielectric constants for all the above sections are determined by a liquid mixture method, in which air film errors are avoided. The details of the method can be known from an earlier communication by the author.[1] The values are determined at a frequency of 1·6 megacycles/sec.

3. Results

The dielectric constants of crystals belonging to the cubic system are given in Table I and those of uniaxial crystals in Table II. The dielectric constants of the two orthorhombic crystals are given in Table III.

Table I

Crystal	Dielectric constant	
	Author	Previous values
Barium nitrate ..	5·7	5·2[2], 4·95[3] (for powder)
Lead nitrate ..	16·0	14·8[2], 16[4], 16·8[5] (for powder)
Rock-salt ..	5·8	6·29[6], 5·60[4], 6·2[8], 5·62[5], 6·36[9], 5·6[3]
Sodium chlorate ..	5·9	5·8[10],
Fluorite Sp. I ..	6·9	6·92[6], 6·70[4], 6·85[8]
Fluorite Sp. II ..	6·95	
Fluorite Sp. III ..	7·0	
Spinel ..	8·6	