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COUMARINS OF Coronilla elegans

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In a chemotoxonomic study of the genus *Coronilla* L. [1], no fewer than six substances of coumarin nature have been detected in the seeds of *C. elegans* Panc. In contrast to other species, the plant investigated contained a substance the Rf value of which in the chloro-form formamide system differed from that of scopoletin. On chromatograms, before treatment with an ethanolic solution of alkali, this compound was detected in the form of faint blue spot, and, after treatment, by a bright yellow fluorescence.

To isolate the coumarins the seeds were ground and extracted with a tenfold amount of 80% ethanol. The extract obtained was evaporated until the solvent has been eliminated, and the residue was mixed with water (1:1) and was treated successively with petroleum ether, chloroform, and ethyl acetate. The petroleum ether extract contained no coumarins and was not investigated further. Not fewer than six substances exhibiting a blue fluorescence in UV light were detected in the chloroform extract.

The substances detected were separated by partition chromatography on a column of silica gel. Formamide was used as the stationary phase and chloforom and benzene and mixtures of them as the mobile phases. When the column was washed with benzene containing 10% of chloroform, a substance was obtained with the empirical formula $C_{19}H_{12}O_7$, mp 254-256°C, $\lambda_{max}C_{2}H_5OH$ 266, 345 nm, which was identified as daphnoretin [2]. When the column was then washed with benzene containing 80% of chloroform, and also with pure chloroform, a substance was isolated with the formula $C_{10}H_8O_4$, mp 185-187°C, $\lambda_{max}C_2H_5OH$ 239, 255, 295, 347 nm. Its IR spectrum showed bands at 1712 cm⁻¹ (α -pyrone) and 2930 cm⁻¹ ($-OCH_3$). When the substance under investigation was demethylated with aluminum chloride, esculetin was formed. A derivative of esculetin is scopoletin (6-methoxyesculetin), but the substance obtained differed from scopoletin by its Rf value, melting point, color, and fluorescence after treatment of chromatograms with an ethanolic solution of caustic soda. It may be assumed that this compound is an isomer of scopoletin — 7-methoxyesculetin.

To confirm this structure we methylated esculin (esculetin $6-O-\beta-D-glucopyranoside)$ with dimethyl sulfate in acetone using anhydrous potassium carbonate as catalyst. The methylation product was hydrolyzed with 5% sulfuric acid, which gave 7-methoxyesculetin ($C_{10}H_8O_4$, mp 185-187°C), identical with the substance isolated from the seeds.

On further elution of the column with chloroform, scopoletin and umbelliferone were isolated [2].

Thus, from *C. elegans* we have isolated four hydroxycoumarins for the first time, and of these it is the first time that isoscopoletin (6-hydroxy-7-methoxycoumarin) has been isolated from the genus *Coronilla*.

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