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Synthesis of Spatheliabischromene

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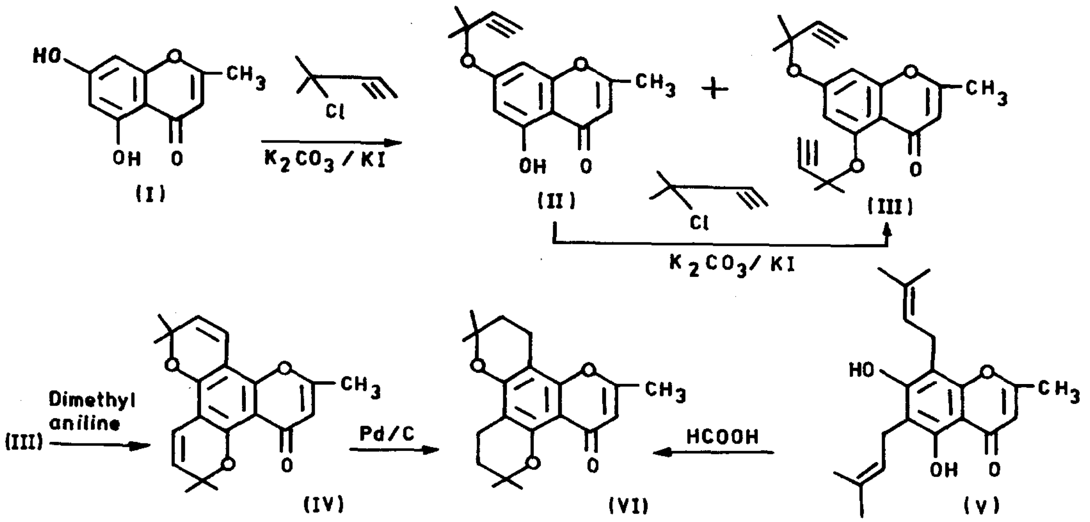
Spatheliabischromene was recently isolated[1,2] from the leaves and stems of *Cneorum tricoccum* L. The structure (IV) assigned to it on the basis of spectral data has now been confirmed by its synthesis.

2-Methyl-5,7-dihydroxychromone (nor-eugenin, I, 1 g) on refluxing for 170 hours with excess of 2-methyl-2-chloro-but-3-yne (1.5 g) in acetone containing freshly ignited potassium carbonate (5 g) and potassium iodide (1 g) yielded a mixture of mono- and di-propargyl ethers (II) and (III) along with unreacted chromone (I) which were separated by column chromatography.

2-Methyl-5,7-dipropargyloxychromone (III) crystallised from n-hexane-benzene mixture as light yellow needles (12 mg), m.p. 128-30°. It gave no colour with alcoholic $FeCl_3$ (confirming the absence of free -OH groups in chromone) (Found: C, 74.1; H, 6.4. $C_{20}H_{20}O_4$ requires C, 74.1; H, 6.2%).

2-Methyl-7-propargyloxy-5-hydroxychromone (II) crystallised from benzene - pet. ether mixture as yellow plates (450 mg), m.p. 153-54° (lit[3]. 153-54°); brown ferric reaction. (Found: C, 69.6; H, 5.4. $C_{15}H_{14}O_4$ requires C, 69.8; H, 5.5%). It was identical (m.m.p.; superimposable IR and co-tlc) with an authentic sample of 2-methyl-7-propargyloxy-5-hydroxychromone. It (II, 450 mg) could be converted to its dipropargyloxychromone (III, 350 mg) by refluxing it with more of 2-methyl-2-chloro-but-3-yne as above for another 150 hrs.

2-Methyl-5,7-dipropargyloxychromone (III) underwent rearrangement on boiling in dimethyl aniline (14 ml) at 200-210° for 3 hours and the product obtained on working up the reaction mixture was purified by column chromatography and subsequently crystallised from pet. ether - ethyl acetate mixture as light yellow solid, m.p. 148-50° (lit.[1] 150-52°; lit.[2] 146-148°). It



was identical (tlc, mixed m.p. and superimposable IR spectrum) with the natural sample of spatheliabischromene (Found: C, 74.2; H, 6.5. $C_{20}H_{20}O_4$ requires C, 74.1; H, 6.2%). λ_{max}^{MeOH} 244, 270, 285 nm. ν_{max}^{KBr} 1660, 1630 cm^{-1} ($>C=O$). NMR($CDCl_3$, δ): 1.48 and 1.52 (2s, 6H each of 2 $>C(CH_3)_2$ groups), 2.26(s, 3H of $-CH_3$ at C_2), 5.62(d, J = 9.5 Hz, 2H, olefinic protons of chromene ring), 5.98(s, 1H in 3-position), 6.68 and 6.75(2d, each having J = 9.5 Hz, two olefinic protons of chromene ring).

Its structure was further confirmed by hydrogenating spatheliabischromene (IV) with Pd-charcoal. The di-(dihydropyrano)-derivative (VI) crystallised from benzene - pet. ether mixture as colourless thick needles, m.p. 155-56° (lit.[4] 155°); was in complete agreement (m.m.p., tlc) with the sample obtained by cyclising 6,8-di-C-prenyl nor-eugenin (V) with formic acid.

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