SYNTHESIS OF 7-HYDROXY-6, 2', 4', 5'-TETRAMETHOXYISOFлавONE


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Abstract

Synthesis of 7-hydroxy-6, 2', 4', 5'-tetramethoxyisoflavone (I) isolated from Pterodon aparicoid has been carried out using the epoxide (IV) of the chalcone (III).

An isoflavone isolated from Pterodon aparicoid was considered to be 7-hydroxy-6, 2', 4', 5'-tetramethoxyisoflavone (I) which was later synthesised by Krishnamurti et al. This communication reports the synthesis of the isoflavone (I) and its 7-methyl ether (II) by method that is more convenient than the earlier method and is based on the biogenetic considerations which suggest chalcones to be the precursors for such compounds. For this purpose 2', 4'-dibenzylxoy-2, 4, 5, 5'-tetramethoxychalcone (III) obtained by the condensation of 2, 4, 5-trimethoxybenzaldehyde with 2, 4-dibenzylxoy-5-methoxyacetophenone, was used as the starting compound. The chalcone (III), when treated with alkaline hydrogen peroxide, gave its epoxide (IV) which on treatment with boron trifluoride-etherate underwent rearrangement as reported earlier in the similar cases, to yield the corresponding α-formylclosbenzoxy which, when directly treated with hydrochloric acid in acetic acid, gave the required isoflavone (I) that was methylated to obtain its 7-methyl ether (II). The synthetic isoflavones (I and II) agreed with the natural sample of the compound and its methyl ether.

Experimental

2', 4'-Dibenzylxoy-2, 4, 5, 5'-tetramethoxychalcone (III):

A solution of 2, 4-dibenzylxoy-5-methoxyacetophenone (2-0 g) and 2, 4, 5-trimethoxybenzaldehyde (1-0 g) in alcohol (30 ml) was treated with potassium hydroxide (1-5 g in 1-5 ml of water) and the resulting reaction mixture was left at room temperature for 48 hrs. On acidification with hydrochloric acid it gave a yellow solid that was filtered and washed. It crystallised from ethanol to give the chalcone (III) as yellow needles (1-5 g), m.p. 146-47° (Found: C, 72.9; H, 5.5. C₃₃H₃₂O₇ required C, 73.3; H, 5.9%).

It did not give any colouration with alcoholic ferric chloride.

2', 4'-Dibenzylxoy-2, 4, 5, 5'-tetramethoxychalcone epoxide (IV):

A solution of the chalcone (III) (1-0 g) in a mixture of acetone (60 ml) and methanol (10 ml) was treated with aqueous sodium hydroxide (2 ml, 8%) and then hydrogen peroxide (2 ml, 30%) was added. The resulting reaction mixture was left overnight at room temperature. On dilution with water (100 ml), the epoxide (IV) separated out as light yellow coloured solid that was filtered, washed with water and then dried. It crystallised from chloroform-petroleum ether as light yellow needles (0-8 g), m.p. 120-21° (Found: C, 71.1; H, 5.6. C₃₃H₃₂O₈ required C, 71.2; H, 5.8%).

7-Hydroxy-6, 2', 4', 5'-tetramethoxyisoflavone (I):

A solution of the epoxide (IV) (0-5 g) in dry benzene (30 ml) was treated with boron trifluoride-etherate (1-0 ml) and then stirred for 1 hr. The reaction mixture was extracted with ether and ethereal layer was washed with water. Removal of the solvent from the extract yielded a residue that was dissolved in glacial acetic acid (100 ml) and then treated with concentrated hydrochloric acid (3 ml). The resulting solution was heated on a boiling water-bath for 2 hrs., cooled and then diluted with water (180 ml). This was extracted with ether and then ethyl acetate. Removal of the solvents from the combined extracts gave a residue which was treated with aqueous sodium carbonate (10%). The sodium carbonate soluble fraction on acidification with hydrochloric acid yielded the required isoflavone (I) that was extracted with ethyl acetate. The isoflavone (I) thus obtained was purified by preparative TLC and then crystallised from ethyl acetate as colourless needles (50 mg), m.p. 202-4° (Found: C, 63.22; H, 5.00. C₁₉H₁₈O₇ required C, 63.68; H, 5.06%). U.V. (CH₃OH) 255, 305, 325 nm. No characteristic shift with NaOAc.

6, 7, 2', 4', 5'-Pentamethoxyisoflavone (II):

A solution of the isoflavone (I) (30 mg) in a mixture of dry ether (15 ml) and dry chloroform (5 ml) was treated with an ethereal solution of diazomethane and then left in the ice-chest for 24 hrs. Removal of the solvent gave a residue that crystallised from ethyl
Acetone-petroleum ether as colourless crystalline solid. m.p. 172-73° (Found: C, 64.32; H, 5.12. C₂₅H₂₅O₂ required C, 64.5; H, 5.4°). U.V. (CH₂OH) 255, 305 nm. N.M.R. (δ, CDCl₃, TMS as internal standard): 3.76-3.90 (15 H, 5 × -OCH₃), 6.58 (1H, s, C₅-H), 6.81 (1H, s, C₅'-H), 6.87 (1H, s, C₅-H), 7.59 (1H, s, C₅-H), 7.81 (1H, s, C₅-H).

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11. —, —, Ibid., 1965, 21, 963.

IMMUNOCYTOCHEMICAL TECHNIQUES FOR LOCALIZATION OF C³ COMPONENT OF THE COMPLEMENT

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C³ COMPONENT of the complement is synthesized and secreted in the blood by visceral organs such as liver, spleen, etc.¹⁻². C³ levels are measured in the blood serum mainly by immunoprecipitation methods. However, no method is available for localization of this component at the site of synthesis in the cells. Nevertheless, C³ component has been shown by ferritin labelling on the erythrocyte membrane involving the formation of immune complexes. In this communication we describe methods for the localization of C³ component in the tissues using monospecific anti-C³ sera raised in rabbits. Cross reactivity of sera from different animals to anti-human C³ was checked by Ouchterlony technique. The central well was loaded with anti-human C³ serum (anti β₁ C₁′; A globulin; Behring Werke, West Germany). The peripheral wells were loaded with sera obtained from monkey, rat, cat, dog, rabbit and human. The plates were incubated in a moist chamber at room temperature and were observed for the precipitin lines after 24 hrs and 48 hrs.

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