FLAVONE FROM ARTEMISIA HERBA-ALBA
A SYNTHETIC STUDY

A new flavone isolated from Artemisia herba-alba was assigned its constitution by Segal et al. as 5, 4'-dihydroxy-6, 7, 3'-trimethoxyflavone had m.p. 147° whereas Morita et al.3 who isolated its 4'-monoglucose from Cirsium lineare, reported that 5, 4'-dihydroxy-6, 7, 3'-trimethoxyflavone had m.p. 208–209°. However, Krishnamurti et al.2 made this compound in some other connection and recorded its m.p. 200–01°. In view of the different melting points reported for the three different samples of the same flavone, its synthesis by another method was considered desirable to settle this discrepancy. For this purpose, 5, 6, 7, 3'-tetramethoxy-4'-benzoylxyflavone obtained by selenium dioxide oxidation of 2'-hydroxy-3', 4', 5', 6'-tetramethoxy-4'-benzoylxyalkane4 when subjected to the catalytic debenzylation and then subsequent selective demethylation yielded 5, 4'-dihydroxy-6, 7, 3'-trimethoxyflavone. This dihydroxytrimethoxyflavone was identical with the sample made by the procedure described by Krishnamurti et al.2.

The natural sample kindly provided by Dr. R. Segal was insufficient for the melting point or mixed melting point determinations which could have settled this discrepancy. Hence the constitution assigned to the flavone isolated1 from A. herba-alba needs revision.

Experimental

5, 6, 7, 3'-Tetramethoxy-4'-benzoylxyflavone.—A mixture of 2'-hydroxy-3', 4', 5', 6'-tetramethoxy-4'-benzoylxyalkane (1.0 g), selenium dioxide (1.7 g), and amyl alcohol (40 ml) was refluxed for 24 hrs and then worked out. The flavone crystallised from benzene-acetone as colourless needles, m.p. 178–79°. Mixed melting point with the sample made by the other method* was unchanged.

5, 6, 7, 3'-Tetramethoxy-4'-hydroxyflavone.—The above benzoylxytetramethoxyflavone (0.5 g) in ethyl acetate (50 ml) and Pd-C (0.3 g) were stirred in an atmosphere of hydrogen till debenzylation completed. 5, 6, 7, 3'-Tetramethoxy-4'-hydroxyflavone crystallised from benzene as colourless needles, m.p. 208–10° (Found: C, 63.3; H, 4.8. \(C_{15}H_{18}O_6\) requires: C, 63.68; H, 5.02%).

5, 4'-Dihydroxy-6, 7, 3'-trimethoxyflavone.—The above monohydroxytetramethoxyflavone (0.3 g) in acetonitrile (5 ml) and aluminium chloride (0.3 g) were refluxed for 4 hrs., and then worked out. The demethylation product crystallised from alcohol as pale yellow needles, m.p. 200–201°. Mixed melting point with the sample obtained by the other method2 was unchanged.
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Krishnamurti et al., have reported the m.p. 144–46°. However this flavone, when made by their method, was found to have m.p. 178–79°.


FRIEDEL-CRAFTS AKLYLATION OF AROMATIC HYDROCARBONS WITH SUBSTITUTED ALICYClic LACTONES

The aluminium chloride-catalysed condensation of aromatic hydrocarbons with simple substituted alicyclic lactones like the lactone of 4-methyl-2-hydroxycyclohexaneacetic acid was found by Chatterjee and Bhattacharya1 to afford a mixture of secondary alkylates consisting of 2-aryl and 3-aryl-4-methylcyclohexaneacetic acid to the exclusion of the tertiary alkylate, e.g., the 4-aryl isomer. The facile rearrangement in the cyclopentane system has also been observed by Chatterjee and coworkers2 who studied the catalysed alkylation of aromatic hydrocarbons with the lactone of cyclopentanol-2-acetic acid. We now report the synthesis of lactone of 4-methyl-2-hydroxycyclopentaneacetic acid (I) and the Lewis acid catalysed alkylation of aromatics with it.

The lactone (I) was prepared from β-methyl adipic acid, m.p. 93°, obtained from 4-methylcyclohexanol by oxidation with 50% nitric acid in the presence of V₂O₅. The diethyl ester, b.p. 130–32/14 mm, on Dieckmann cyclisation furnished 4-methyl-2-carboxy-cyclopentanone, b.p. 90–92/1 mm, which on alkylation by ethyl chloroacetate in the presence of sodium ethoxide afforded ethyl 4-methyl-2-carboxy-2-acetate, b.p. 132–35/0.5 mm. This on hydrolysis by 1:1 HCl yielded 4-methylcyclopentane-2-one-1-acetic acid, b.p. 155–60/2 mm., semicarbazone, m.p. 210°, which on NaOCl reduction gave a stereoisomeric mixture of the desired lactone (I), b.p. 95–100°/1 mm, nD₅ 1.4650, a major amount of the trans variety.3

The Friedel-Crafts condensation of the lactone (I) with benzene in the presence of AlCl₃ gave as expected a secondary alkylate consisting of a stereoisomeric mixture of 4-methyl-2-phenylcyclopentaneacetic acid (II), b.p. 155–57/0.6 mm as the exclusive product, isolated through the ethyl ester, b.p. 140–41/0.6 mm in 78% yield together with a small amount of 3-methylcyclopentaneacetic acid formed by hydride transfer and consequent reduction of the

\[
\text{H}_3\text{C} \quad \text{H}_3\text{C} \\
\text{O} \quad \text{O} \\
\text{CO}_2\text{H} \quad \text{O} \\
\text{H}_3\text{C} \quad \text{H}_3\text{C} \\
\quad \quad (\text{I}) \quad (\text{II}) \quad (\text{III})
\]

lactone (I). The acid (II) on PPA cyclisation afforded 2-methyl-6-keto 6, 7, 8, 9-tetrahydro-4, 5-benzindane (III), b.p. 137–38/1 mm. semicarbazone m.p. 206°. DNP derivative m.p. 209° as a stereoisomeric mixture. The structure of the ketone was confirmed by its reduction and dehydrogenation of 2-methyl-4, 5-benzindane, picro m.p. 91° TNB complex m.p. 103° as well as by its unequivocal synthesis starting from ethyl 4-methylcyclopentane-2-one-1-acetate and phenyl lithium followed by Paar reduction of the resulting lactone and cyclisation.

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ISOLATION OF A-AMYRIN STEARATE, β-AMYRIN AND LUPENOL PALMITATES FROM THE COSTUS LEAVES

The isolation of taraxasterol and its acetate from the hexane extract of the leaves (and stalks) of the costus plant, Swainsona Lappa clarke, has been reported. By chromatography of the hexane extract over alumina and silver nitrate impregnated silicic acid, followed by crystallisation of some of the fractions, three low melting esters A, B, C have been isolated in the pure state. These have been identified as a-amyrin stearate, β-amyrin palmitate and lupenol palmitate respectively, by chemical reactions and comparison of physical constants and spectral data with those reported in literature.4,5 α-β-γ-1 Ster A, C₂₁H₃₄O₄ m.p. 46–48° (TIOH+Me₂CO; 1:3) (α), 81° (benzene, c, 1:84). On saponification, yields seastic acid, C₁₉H₂₂O₄, M¹ 284, m.p. 69° (TIOH and α-amyrin (I), C₂₀H₂₀O₂, M¹ 426, m.p. 181° (hexane i 10°).