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NEW NATURAL CHALCONES FROM <u>FLEMINGIA</u> <u>CHAPPAR</u> HAM.[1]

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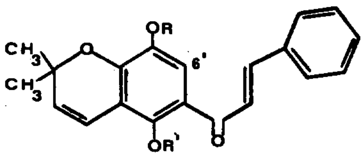
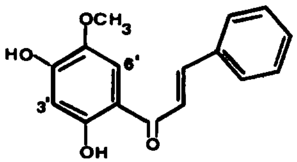
The recent claim[2] of isolation of new chalcones of yet undisclosed structure from Flemingia chappar Ham. (Leguminosae) prompts us to report our results on the same subject. Four chalcones were isolated from the ethereal extract of the flowers or the leaves and purified by chromatography through silica gel with hexane/AcOEt. Two of them were identified with the known 2',4'-dihydroxychalcone[3] and 2',4',4-trihydroxychalcone from m.ps., spectra and comparison with authentic samples. The two other chalcones appeared to be new. The former (I),m.p. 191-92° (benzene/Hexane),UV max at 300,324 sh and 357 nm in EtOH (ε 11100, 7250, 8700),exhibited a molecular peak at 322 m/e in the mass spectrum,with most important fragmentation peaks at 307 ($M - CH_3$) and 203 ($M - CH_3 - C_8H_8$) m/e,which indicated an unsubstituted A ring. The NMR spectrum (60 MHz, $CDCl_3$) of I show a singlet of 6 H at 1.50,an AB system of 2 H at 5.58 and 6.76 (J=10) and an absorption for 8 H between 7.2 and 8.0 δ, including a singlet at 7.35δ and the chalcone double bond protons. Two OH appeared at 5.11 and 13.60 δ. Thus the ring B of I must be substituted with a 2,2-dimethylchromene ring and two OH , one of them ortho to the chalcone CO. The chemical shift of the proton in position 4 of the chromene suggested that it was peri to a OH[4],and that this was the chelated one was confirmed by effect of acetylation[4]. Reaction of I with Ac_2O and AcONa for 5 min. on a water bath gave the monoacetate II,where the chromene protons (5.69 and 6.75 δ) and the chelated OH (13.60 δ) were unaltered; reflux with the same reagents for 2 hrs. yielded the diacetate III,with the CH=CH protons now at 5.71 and 6.40



I R = R' = H
II R = Ac R' = H
III R= R' = Ac



IV

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($\Delta\delta = 0.36$ for the proton 4)[4]. The position of the other OH must be 5',because of the chemical shift of the only proton on ring B (7.35 δ , *ortho* to the CO)[5], and the absence of any $J_{4,8}$ long-range coupling in the chromene ring[4]. Thus the substitution of ring B and the structure of I were established. Synthetic I was obtained in low yields by condensation of benzaldehyde with 2,2-dimethyl-5,8-dihydroxy-6-acetylchromene[6] in 50% KOH at 100° for 10 min. It was identical with the natural compound on TLC and spectral behaviour.

The other new chalcone (IV), m.p. 157-59° (benzene/hexane), UV max. at 314 and 384 nm in EtOH (ϵ 10000, 18300), with a molecular peak at 270 m/e in the mass spectrum,and peaks at 255 ($M - CH_3$), 239 ($M - OCH_3$), 193 ($M - C_6H_5$), 166 ($M - C_8H_8$), 151 ($M - CH_3 - C_8H_8$), was also an unsubstituted ring A chalcone. The NMR spectrum (60 MHz, acetone-d_6) show a OCH_3 at 3.90, a singlet at 6.42 (1 H) and 8 H between 7.30 and 8.05δ . Two OH appeared at 7.7 and 13.50δ . The conclusion followed that the two H on ring B must be *para*, and the high-field singlet at 6.42 must be arise from the proton in 3' position (between two OR) and the proton giving the low-field signal must be in 6', *ortho* to the CO) (compare the values 6.49 and 7.20 in V).

This established the structure of IV,except for the uncertainty of the ralative position of the free OH and the OCH_3 (4' or 5'). Degradation of IV with barium hydroxide gave the known 2,4-dihydroxy-5-methoxyacetophenone V, which with benzaldehyde in alkaline solution gave synthetic IV. The isomer 2',5'-dihydroxy-4'methoxychalcone was also prepared and found to be different from IV.

The rather unusual 1,2,4 hydroxylation pattern of ring B in both *Flemingia chappar* chalcones is exactly the same as that so far found only in Wars pigments flemingins and homoflemingins[5] (from *Flemingia rhodocarpa* Baker) and in stillopsin[7] (or neoplathymetin[8]). It is thus possible that some *Flemingia* species have the peculiar ability to introduce hydroxyls *para* to those coming from the usual biosynthesis via acetate.

A rhamnoside of quercetin (most probably quercitrin) was obtained from the methanol extract of the flowers. No chalcone was found in the leaves and stems of the related species *Flemingia strobilifera*.

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