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SYNTHESIS OF CARPACHROMENE AND RELATED ISOPENTENYLATED DERIVATIVES OF APIGENIN

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Abstract—Acacetin (4) on reaction with prenyl bromide in the presence of methanolic sodium methoxide yielded 6,8-di-C-prenyl-(5) and 6-C-prenyl-(10) derivatives. The former (5) formed the correspoonding bisdihydropyrano derivative (8). Monomethyl derivative of 10 (12) gave monodihydropyrano derivative (13). DDQ reaction of 10 followed by methylation afforded di-O-methyl carpachromene (2); whereas that of 5 gave a mixture of 21 and 22.

Nuclear prenylation of apigenin (3) in a similar way gave 6,8-di-C-C-prenyl-(16), its 7-O-prenyl-(15) and 6-C-prenyl-(18) derivatives. DDQ reaction of 18 provided natural carpachromene.[1] The structure of the isopentyl-ated apigenin isolated by Dreyer *et al.*[2] needs further consideration.

From the leaves of *Flinderis leavicarpa* (Rutaceae), carpachromene was isolated by Picker *et al.*[1] and shown to be 5 - 4' - dihydroxy - 6",6" dimethylpyrano(2",3":7,6) flavone (1) on the basis of the UV, IR and NMR spectra of its acetate and dimethyl ether (2) together with alkaline degradation of the dimethyl ether to evodionol and anisic acid. The linear 2,2-dimethylpyrano structure for carpachromene was deduced from the effect of acetylation on chemical shifts of protons at 4" and 5" positions and also from NOE measurements on its dimethyl ether.

Before the isolation of carpachromene, Dreyer and Park[2] had reported isolation of a compound having the same structure (1) from the foliage of *Pamburus missionis*. However, a comparison of the m.ps, UV, NMR and mass spectroscopic data of the two natural compounds and their acetates shows some differences. Although Picker *et al.*[1] have given sufficient data to prove the structure of carpachromene, the evidence given by Dreyer and Park[2] for their natural product is less comprehensive. Therefore unambiguous syntheses of 1 and 2 were projected to establish the structures of the two natural compounds.

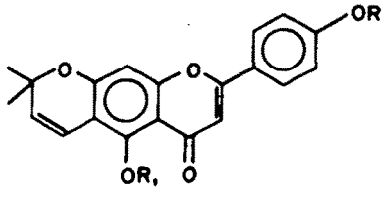
A biogenetic-type synthesis of 1 consisting of nuclear prenylation of apigenin (3) in the 6-position and subsequent cyclodehydrogenation was undertaken. But to make the identification of the nuclear prenylation products of apigenin easier, the nuclear prenylation of acacetin (4) was first studied.

Acacetin (4) when heated with prenyl bromide in the presence of methanolic sodium methoxide, yielded a mixture of two products. The major product proved to be 6,8 - di - C - prenyl derivative (5) on the basis of the formation of the diacetate (6) (NMR: 2s, δ 2.30 and 2.40) and monomethyl ether (7) (NMR: 2s, δ 3.75 and 3.83), along with the absence of aromatic protons of ring A in any of these compounds (5 to 7).

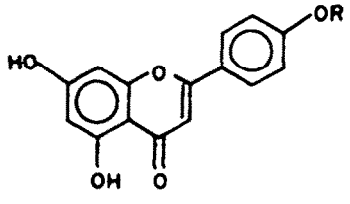
The structure 5 was further confirmed by the acid cyclisation of 5 to a bisdihydropyran (8) and of 7 to a mono C-prenyl-monodihydropyran (9). The structures 8 and 9 were supported by their NMR spectra. Thus 8 showed resonance signals of four methylene groups as triplets (1.80, 2.65 and 2.92), whereas 9 had signals of one C-prenyl unit (2s, 1.38 and 1.45; d, 3.00 and m, 5.05–5.25) and one condensed dihydropyran unit (two triplets, 1.78 and 2.75).

The minor fraction of the above prenylation mixture was identified as 6-C-prenylacacetin (10). In conformity, the compound formed a diacetate (11) and also a monomethyl ether (12) showing positive ferric reaction. Further all these three compounds showed NMR bands from only one C-prenyl unit and one proton of ring A. The orientation of the C-prenyl unit in 10 was confirmed by acid cyclisation of monomethyl ether 12, when the corresponding chroman 13 resulted. Had it been a 8-C-prenyl isomer, the cyclisation could not have occurred. Further C-prenylation of 5,7-dihydroxyflavones with prenyl bromide in the presence of methanolic sodium methoxide has always yielded the corresponding 6-C-prenyl derivative.[3,5]

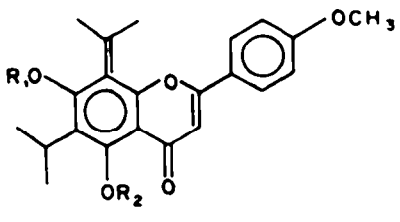
Cyclodehydrogenation of 6-C-prenyl acacetin (10) with DDQ, gave the corresponding 2,2-dimethylpyran (14) which showed characteristic doublets of H_{α} and H_{β} at 6.75 and 5.65 (J = 10 Hz). When 14 was methylated with dimethylsulphate, it afforded 5,4' - dimethoxy - 6",6" - dimethylpyrano(2",3":7,6) flavone (2) identical in m.p., NMR and UV data with carpachromene dimethyl ether.



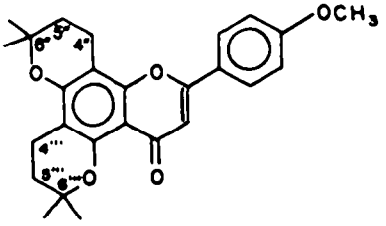
1: R = R, = H, Carpachromene
2: R = R, = Me
14: R = Me, R, = H
23: R = R, = Ac



3: R = H
4: R = Me



5: $R_1 = R_2 = H$
6: $R_1 = R_2 = Ac$
7: $R_1 = Me$; $R_2 = H$



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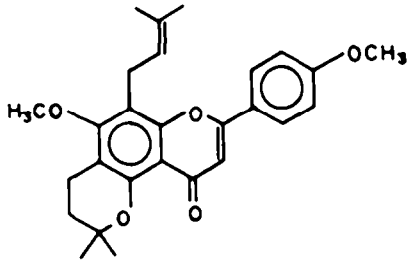

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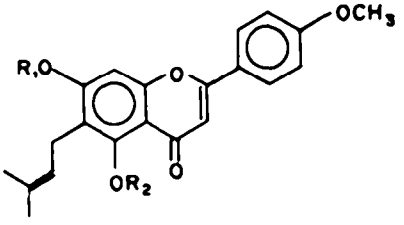
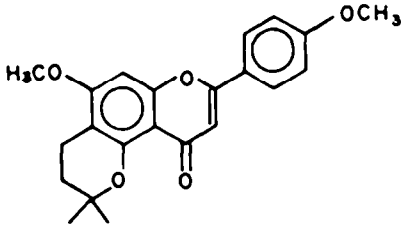


10: $R_1 = R_2 = H$
11: $R_1 = R_2 = Ac$
12: $R_1 = Me$; $R_2 = H$



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This establishes that the structure of carpachromene given by Picker *et al.*[1] is correct.

In order to synthesise carpachromene (1) itself, apigenin (3) was prenylated in the same manner as acacetin. It yielded a mixture of three products. The major product was identified as 7 - 0 - prenyl - 6,8 - di - C - prenyl apigenin (15) on the basis of its NMR spectrum (Experimental) and the formation of 6,8-di-C-prenyl apigenin (16) on heating with 50% aqueous morpholine.[6] The orientation of the O-prenyl group in the 7-position was established by a study of its UV spectrum in methanol which showed no marked shift as compared with sodium acetate.

The second product was characterised as 6,8 - di - C - prenyl apigenin (16) by the formation of triacetate (17) and the identity of the dimethyl ether (7) with the compound prepared from acacetin. The third nuclear prenylation product was established as 6 - C - prenyl-apigenin (18) on the basis of the formation of triacetate (19) and the identity of its dimethyl ether with 9. All these compounds exhibited the appropriate NMR spectra.

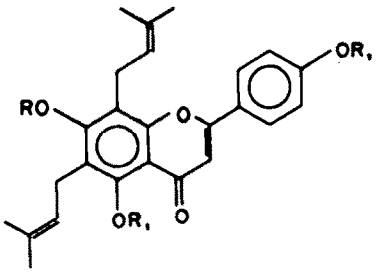
6-C-Prenylapigenin (18) when cyclodehydrogenated with DDQ afforded the corresponding 2,2-dimethylpyran (1) identical in all respects (m.p., UV, diacetate and NMR) with natural carpachromene. Hence it is established beyond doubt that carpachromene is the linear isomer (1) as stated by Picker *et al.*[1]

Since the isopentenylated apigenin isolated by Dreyer *et al.*[2] differs from the synthetic compound 1, it may be the angular isomer 20.

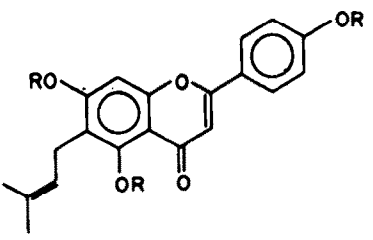
6,8-Di-C-prenylacacetin (5) was also cyclodehydrogenated with DDQ with the idea that the resulting two possible pyranoflavones (21 and 22) may also be discovered either as such or as corresponding de-O-Me compounds in nature as in the case of other flavonoids.[3,5] These flavones (21 and 22) have been fully characterised and their mass spectra identify which is linear and which is angular. Thus the linear isomer (21) showed an $(M-55)^+$ peak; whereas the angular one (22) showed an $(M-56)^+$ peak.[7]

EXPERIMENTAL

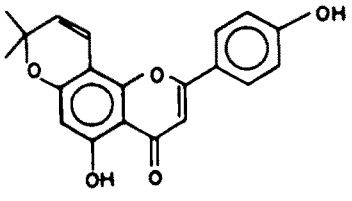
All m.ps are uncorrected; unless stated otherwise, all UV spectra were taken in MeOH (figures in parenthesis are log ϵ values); NMR spectra were recorded on BS487C spectrometer (80 MHz) in $CDCl_3$ with reference to TMS as an internal standard; the chemical shifts are expressed in δ values; light petroleum ether used had boiling range 60°–80°; silica gel was



15: R = Me_2C—CH—CH_2—; R_1 = H
16: R = R_1 = H
17: R = R_1 = Ac



18: R = H
19: R = Ac



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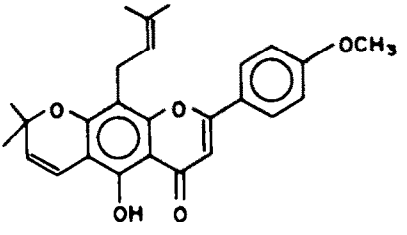

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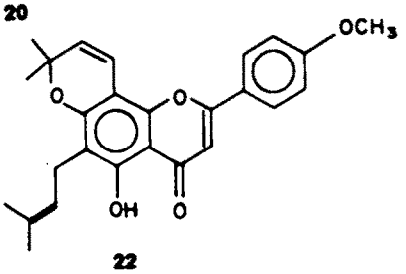

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used for column chromatography and silica gel G for TLC; R_f values are recorded for TLC using one of the following solvent systems: (A) toluene:ethylformate:formic acid (5:4:1), (B) benzene: ethyl acetate (15:85), (C) benzene:ethyl acetate (1:4); spraying of TLC plates was carried out with 10% aq. H_2SO_4 and/or 1% ethanolic $FeCl_3$.

Nuclear prenylation of acacetin (4)

To a soln of 4[6] (4.4 g) in anhyd MeOH (140 ml) was added methanolic NaOMe (5.6 g of Na in 60 ml MeOH). The resulting soln was cooled, treated with prenyl bromide (7.6 ml) and then refluxed for 4 hr. The solvent was distilled *in vacuo* and the residue treated with ice and dil. HCl. The solid was collected and subjected to column chromatography and the column eluted successively with (1) light petroleum:benzene (1:1), (2) benzene alone and (3) EtOAc:benzene (1:20) giving the following three fractions A–C.

Fraction A crystallised from MeOH yielding 5 as yellow plates (0.7 g), m.p. 200–1°; soluble in Na_2CO_3 aq; dark brown ferric reaction; R_f 0.65 (solvent B). (Found: C, 74.5; H, 6.9. $C_{26}H_{28}O_5$ requires: C, 74.3; H, 6.7%); λ_{max} 226, 283 and 329 nm (4.38, 4.36 and 4.29 respectively); NMR spectrum (60 MHz): 1.74 and 1.82 (2s, 12 H, two $(CH_3)_2C$=), 3.46 and 3.62 (2d, J = 10 Hz, 4 H, two Ar–CH_2), 3.85 (s, 3 H, OCH_3), 5.1–5.4 (m, 2 H, two –CH=), 6.48 (s, 1 H, H-3), 6.94 (d, J = 9.5 Hz, 2 H, H-3' and 5'), 7.73 (d, J = 9.5 Hz, 2 H, H-2' and 6') and 11.98 ppm (s, 1 H, of chelated OH). The diacetate (3) prepared by the Ac_2O-pyridine method crystallised from MeOH as colourless plates, m.p. 190–91°; R_f 0.5 (solvent C). (Found: C, 71.3; H, 6.8. $C_{30}H_{32}O_7$ requires: C, 71.4; H, 6.3%). λ_{max} 230, 266 and 323 nm (4.41, 4.31 and 4.47 respectively); NMR spectrum: 1.68, 1.70 and 1.75 (3s, 12 H, two $(CH_3)_2C$=), 2.30 and 2.40 (2s, 6 H, two CH_3CO_2–), 3.2 and 3.45 (2d, J = 6.5 Hz, 4 H, two Ar–CH_2), 3.83 (s, 3 H, OCH_3), 4.88–5.19 (m, 2 H, two –CH=), 6.51 (s, 1 H, H-3), 6.9 (d, J = 9 Hz, 2 H, H-3' and 5') and 7.73 ppm (d, J = 9 Hz, 2 H, H-2' and 6').

Fraction B crystallised from benzene to give 10 as light yellow crystals (0.45 g), m.p. 221–22°; soluble in Na_2CO_3 aq, brown ferric reaction, R_f 0.5 (solvent B). (Found: C, 71.3; H, 5.9. $C_{21}H_{20}O_5$ requires: C, 71.6; H, 5.7%); λ_{max} 220, 250 and 330 nm (4.10, 4.42 and 4.34 respectively). The diacetate (11) prepared from 10 by the Ac_2O-pyridine method crystallised from MeOH as colourless crystals, m.p. 164–65°; R_f 0.41 (solvent C). (Found: C, 68.3; H, 5.82. $C_{25}H_{24}O_7$ requires: C, 68.8; H, 5.5%); λ_{max} 242, 251 and 311 nm (3.92, 4.21 and 4.24 respectively); NMR spectrum: 1.37 (s, 6 H, $(CH_3)_2C$=), 2.38 and 2.48 (2s, 6 H, two CH_3CO_2–), 3.3 (d, J = 7 Hz, 2 H Ar–CH_2), 3.87 (s, 3 H, OCH_3), 5.12 (t, J = 7 Hz, 1 H, –CH=), 6.55 (s, 1 H, H-3), 6.80 (s, 1 H, H-8), 6.97 (d, J = 9 Hz, 2 H, H-3' and 5') and 7.75 (d, J = 9 Hz, 2 H, H-2' and 6').

Fraction C crystallised from acetone-light petroleum mixture to afford acacetin (1 g).

6,8 - Di - C - prenyl - 5 - hydroxy - 7,4' - dimethoxyflavone (7)

A soln of 5 (0.2 g) in acetone (40 ml) was refluxed with Me_2SO_4 (0.06 ml) and ignited K_2CO_3 (1 g) for 3 hr. Acetone was distilled off and water added to the residue. The solid was dried and crystallised from EtOAc when 7 formed light yellow crystals (0.18 g), m.p. 146°; brownish ferric reaction; R_f 0.8 (solvent B). (Found: C, 74.9; H, 7.3. $C_{27}H_{32}O_5$ requires: C, 74.9; H, 7.0%); λ_{max} 229, 288 and 325 nm (3.32, 4.35 and 4.36 respectively); NMR spectrum: 1.65 and 1.76 (2s, 12 H, two $(CH_3)_2C$=), 3.25 and 3.50 (2d, J = 7 Hz, 4 H, two Ar–CH_2), 3.75 and 3.83 (2s, 6 H, two OCH_3), 5.20 (t, J = 7 Hz, 2 H, two –CH=), 6.50 (s, 1 H, H-3), 6.95 (d, J = 9 Hz, 2 H, Ha3' and 5'), 7.75 (d, J = 9 Hz, 2 H, H-2' and 6'), and 13.38 ppm (s, 1 H, chelated OH).

6",6",6"",6"" - Tetramethyl - 4",5":4"",5"" - bis - (dihydropyrano) [2",3":7,8,2"",3"":5,6] - 4' - methoxyflavone (8)

A soln of 5 (0.2 g) in formic acid (20 ml) was heated on a steam bath for 2 hr. After leaving it overnight at room temp. it was poured over ice. The solid was collected and purified by column chromatography. Elution with benzene:EtOAc (20:1) gave 8 which crystallised from EtOAc:light petroleum mixture as colourless crystals (0.1 g), m.p. 199–200°; R_f 0.4 (solvent C). (Found: C, 74.7; H, 6.7. $C_{36}H_{36}O_5$ requires: C, 74.3; H, 6.7%); λ_{max} 261, 280 and 328 nm (3.94, 4.20 and 4.15 respectively); NMR spectrum: 1.38 and 1.42 (2s, 12 H, two $(CH_3)_2C$=), 1.80 (t, J = 7 Hz, 4 H, two Ar-CH_2-CH_2), 2.65 and 2.92 (2t, J = 7 Hz, 4 H, two AR-CH_2-CH_2), 3.85 (s, 3 H, OCH_3), 6.55 (s, 1 H, H-3), 6.97 (d, J = 9 Hz, 2 H, H-3' and 5') and 7.82 (d, J = 9 Hz, 2 H, H-2' and 6').

8 - C - Prenyl - 7,4' - dimethoxy - 6",6" - dimethyl - 4",5" - dihydropyrano [2",3":5,6] flavone (9)

A soln of 7 (0.1 g) in formic acid (15 ml) was heated on a steam bath for 2 hr. The mixture was diluted with water and extracted with $CHCl_3$. The organic layer was evaporated to dryness and the residue crystallised from EtOAc: light petroleum mixture when 9 was obtained as cream coloured crystals (0.08 g), m.p. 204–5°; R_f 0.4 (solvent A). (Found: C, 74.4; H, 7.5. $C_{27}H_{30}O_5$ requires: C, 74.9; H, 7.0%); λ_{max} 225, 272 and 319 nm (4.26, 4.38 and 4.32 respectively); NMR spectrum: 1.25 (s, 6 H, $(CH_3)_2C$), 1.38 and 1.45 (2s, 6 H, $(CH_3)_2C$=), 1.78 (t, J = 7 Hz, 2 H, Ar-CH_2CH_2), 2.75 (t, H = 7 Hz, 2 H, Ar-CH_2-CH_2), 3.00 (d, J = 8 Hz, 2 H, Ar-CH_2-CH=), 3.82 (s, 6 H, OCH_3), 5.05–5.25 (m, 1 H, -CH=), 6.50 (s, 1 H, H-3), 6.95 (d, J = 9 Hz, 2 H, H-3' and 5') and 7.80 (d, J = 9 Hz, 2 H, H-2' and 6').

6 - C - Prenyl - 5 - hydroxy - 7,4' - dimethoxyflavone (12)

An acetone soln of 10 (0.2 g) was refluxed with Me_2SO_4 (0.06 ml) and anhyd K_2CO_3 (1 g) for 3 hr. The product crystallised from MeOH to give 9 as light yellow crystals (0.18 g), m.p. 166–67°; light bluish ferric reaction; R_f 0.80 (solvent B). (Found: C, 72.4; H, 6.6. $C_{22}H_{22}O_5$ requires: C, 72.1; H, 6.0%); λ_{max} 221, 251 and 325 nm (4.12, 4.19 and 4.32 respectively); NMR spectrum: 1.70 and 1.80 (2s, 6 H, $(CH_3)_2C$=), 3.37 (d, J = 8 Hz, 2 H, Ar-CH_2), 3.85 and 3.89 (2s, 6 H, two OCH_3), 5.23 (t, J = 8 Hz, 1 H, -CH=), 6.47 (s, 1 H, H-3), 6.60 (s, 1 H, H-8), 6.97 (d, J = 9 Hz, 2H, H-3' and 5') and 7.85 (d, J = 9 Hz, 2 H, H-2' and 6').

7,4' - Dimethoxy - 6",6" - dimethyl - 4",5" - dihydropyrano [2",3":5,6] flavone (13)

A soln of 12 (0.1 g) in formic acid (15 ml) was heated for 1 hr. The product crystallised from acetone-light petroleum mixture to give 13 as colourless crystals (0.08 g), m.p. 241–2°. (Found: C, 71.8; H, 6.4. $C_{22}H_{22}O_5$ requires: C, 72.1; H, 6.0%); λ_{max} 223, 256 and 324 nm (4.01, 3.98 and 4.27 respectively); NMR (90 MHz) spectrum: 1.35 and 1.41 (2s, 6 H, $(CH_3)_2C$), 1.82 (t, J = 7.5 Hz, 2 H, Ar-CH_2-CH_2), 2.70 (t, J = 7.5 Hz, 2 H, Ar-CH_2-CH_2), 3.82 (s, 6 H, two OCH_3), 6.39 (s, 1 H, H-3), 6.41 (s, 1 H, H-8), 6.97 (d, J = 9 Hz, 2 H, H-3' and 5') and 3.80 (d, J = 9 Hz, 2H, H-2' and 6').

5 - Hydroxy - 4' - methoxy - 6",6" - dimethylpyrano [2",3":7,6] flavone (14)

To a soln of 10 (0.2 g) in dry benzene (30 ml) was added DDQ (0.15 g) and the mixture refluxed for 1 hr when colourless hydroquinone separated out. The mixture was filtered while hot and the filtrate evaporated to dryness. The residue was purified by column chromatography carrying elutions with benzene:light petroleum (1:1). The product crystallised from MeOH to afford 14 as pale yellow crystals (0.12 g), m.p. 169–170°; violet ferric reaction; R_f 0.80 (solvent B). (Found: C, 72.3; H, 5.57. $C_{21}H_{18}O_5$ requires: C, 72.0; H, 5.2%); λ_{max} 225, 254 and 332 nm (4.08, 4.41 and 4.44 respectively); NMR spectrum: 1.50 (s, 6 H, $(CH_3)_2C$), 3.90 (s, 3 H, OCH_3), 5.65 (d, J = 10 Hz, 1 H, H-5"), 6.42 (s, 1 H, H-3), 6.57 (s, 1 H, H-8), 6.75 (d, J = 10 Hz, 1 H, H-4"), 6.97 (d, J = 9 Hz, 2 H, H-3' and 5'), 7.62 (d, J = 9 Hz, 2 H, H-2' and 6') and 13.07 (s, 1 H, chelated OH).

5,4' - Dimethoxy - 6",6" - dimethylpyrano [2",3":7,6] flavone (5,4' - di - O - methylcarpachromene, (2)

The above flavone (14, 0.08 g) in acetone (15 ml) was refluxed with Me_2SO_4 (0.02 ml) and ignited K_2CO_3 (0.3 g) for 6 hr. The product crystallised from acetone–light petroleum mixture to give 2 as light yellow crystals (0.07 g), m.p. 155–56° (lit.[1] m.p. 156°); R_f 0.5 (solvent B). (Found: C, 72.3; H, 5.9. Calc. for $C_{22}H_{20}O_5$: C, 72.5; H, 5.5%); λ_{max} 223, 264 and 321 nm (4.5, 4.2 and 4.25 respectively); NMR spectrum: 1.47 (s, 6 H, $(CH_3)_2C$), 3.83 and 3.84 (2s, 6 H, two OCH_3), 5.6 (d, J = 10 Hz, 1 H, H-5"), 6.35 (s, 1 H, H-3), 6.73 (d, J = 10 Hz, 1 H, H-4"), 6.85 (s, 1 H, H-8), 6.98 (d, J = 9 Hz, 2 H, H-3' and 5') and 7.98 (d, J = 9 Hz, 2 H, H-2' and 6'). In all these properties it agrees with those recorded for carpachromene dimethyl ether.[1]

Nuclear prenylation of apigenin

A soln of 3 (3 g) in anhyd MeOH (105 ml) was refluxed with prenyl bromide (5.7 ml) and a methanolic soln of NaOMe (4.2 g Na in 45 ml MeOH) for 4 hr. Column chromatography of the product and elution successively with (1) benzene:light petroleum (1:1), (2) benzene alone, (3) benzene:EtOAC (95:5) and (4) benzene:EtOAc (85:15) yielded four fractions A–D.

Fraction A crystallised first from benzene:light petroleum and then from MeOH to give 15 as yellow crystals (0.7 g), m.p. 161–62°; bluish ferric reaction; soluble in Na_2CO_3 aq; R_f 0.9 (solvent A). (Found: C, 76.2; H, 6.9. $C_{20}H_{18}O_5$ requires: C, 75.9; H, 7.2%); λ_{max} 221, 272 and 331 nm (3.91, 4.21 and 4.34 respectively); NMR spectrum: 1.77 and 1.82 (2s, 18 H, three $(CH_3)_2C$=), 3.40 and 3.52 (2d, J = 7 Hz, 4 Hz, 4 H, two Ar-CH_2-CH=), 4.50 (d, J = 7 Hz, 2 H, O-CH_2), 5.08–5.5 (m, 3 H, three -CH=), 6.50 (s, 1 H, H-3), 6.97 (d, J = 9 Hz, 2 H, H-3' and 5'), 7.82 (d, J = 9 Hz, 2 H, H-2' and 6') and 13.05 (s, 1 H, chelated OH).

This flavone 15 (0.5 g) was refluxed with 50% aq morpholine (20 ml) for 15 hr. The mixture was treated with dil HCl (1:1) (50 ml) and extracted with ether. The ethereal soln was evaporated to dryness and the residue was purified by column chromatography. Elution with $CHCl_3$ gave 16 which crystallised from EtOAc:light petroleum mixture as yellow crystals (0.2 g), m.p. 190–91°; brownish ferric reaction; R_f 0.8 (solvent A). (Found: C, 74.2; H, 6.7. $C_{25}H_{26}O_5$ requires: C, 73.8; H, 6.5%); λ_{max} 270 and 330 nm (4.22 and 4.24 respectively); NMR spectrum: 1.50 and 1.70 (2s, 12 H, two $(CH_3)_2C$=), 2.80 and 3.12 (2d, J = 7 Hz, 4 H, two Ar-CH_2), 5.02–5.25 (m, 2 H, two -CH=), 6.75 (s, 1 H, H-3), 7.05 (d, J = 9 Hz, 2 H, H-3' and 5') and 7.70 ppm (d, J = 9 Hz, 2 H, H-2' and 6').

The triacetate (17) prepared by Ac_2O-pyridine method crystallised from MeOH as white plates, m.p. 172-73°; R_f 0.6 (solvent B). (Found: C, 70.8; H, 6.4. $C_{31}H_{32}O_8$ requires: C, 70.6; H, 6.5%); λ_{max} 254 and 320 nm (3.92 and 4.21 respectively).

Fraction B crystallised from EtOAc:light petroleum mixture to yield 16 as yellow crystals (0.02 g), m.p. and m.m.p. with the above sample 190–91°. The dimethyl ether 7 prepared from 16 by methylation was also identical with the sample prepared above.

Fraction C crystallised from EtOAc to afford 18 as deep yellow fluffy solid (0.2 g), m.p. 290–91°; violet ferric reaction; R_f 0.55 (solvent A). (Found: C, 70.9; H. 5.7. $C_{20}H_{16}O_5$ requires: C, 71.0; H, 5.3%); λ_{max} 237, 276 and 331 nm (4.01, 4.28 and 4.25 respectively); NMR (DMSO-d_6) spectrum: 1.65 and 1.70 (2s, 6 H, $(CH_3)_2C$=), 3.00 (d, J = 8 Hz, 2 H, $ArCH_2$), 5.05–5.27 (m, 1 H, -CH=), 6.25 (s, 1 H, H-3), 6.62 (s, 1 H, H-8), 6.92 (d, J = 9 Hz, 2 H, H-3' and 5'), 7.80 (d, J = 9 hz, 2 H, H-2' and 6') and 10.25 ppm (s, 1 H, chelated OH). The dimethyl ether (12) was identical in m.p. and m.m.p. and TLC with the sample prepared above. The triacetate (19) prepared by the Ac_2O-pyridine method crystallised from MeOH as colourless crystals, m.p. 262–63°; R_f 0.64 (solvent B). (Found: C, 67.4; H, 5.2. $C_{26}H_{24}O_8$ requires: C, 67.3; H, 5.2%); λ_{max} 240, 281 and 321 nm (3.98, 4.01 and 4.20 respectively).

Fraction D crystallised from acetone to give the starting compound *viz* apigenin (0.8 g).

5,4' - Dihydroxy - 6",6" - dimethylpyrano [2",3":7,6] flavone (carpachromene 1)

A soln of 18 (0.2 g) in dry benzene (100 ml) was refluxed with DDQ (0.15 g) for 2 hr. The product on column chromatography and elution with benzene:EtOAc (9:1) gave a yellow solid which crystallised from EtOAc as yellow crystals (0.1 g), m.p. 239–40° (lit.[1] m.p. 239–41°), dark violet ferric reaction. (Found: C, 71.1; H, 4.8. $C_{20}H_{16}O_5$ requires: C, 71.4; H, 5.0%); λ_{max} 235, 310 and 332 nm (4.42, 4.50 and 4.41 respectively); NMR (DMSO-d_6) spectrum: 1.40 (s, 6 H, $(CH_3)_2C$<), 5.65 (d, J = 10 Hz, 1 H, H-5"), 6.27 (s, 1 H, H-3), 6.40 (d, J = 10 Hz, 1 H, H-4"), 6.58 (s, 1 H, H-8), 6.75 (d, J = 9 Hz, 2 H, H-3' and 5'), 7.23 (d, J = 9 Hz, 2 H, H-2' and 6') and 9.75 (s, 1 H, chelated OH). The diacetate (23) prepared by the Ac_2O-pyridine method crystallised from MeOH as colourless crystals; m.p. 240–41° (lit.[1] m.p. 239–41°). (Found: C, 69.0; H, 5.2. $C_{24}H_{20}O_7$ requires: C, 68.6; H, 4.8%); λ_{max} 220, 263 and 314 nm (4.4, 4.39 and 4.32 respectively); NMR ($CDCl_3$ + CD_3COCD_3) spectrum: 1.44 (s, 6 H, $(CH_3)_2C$<), 2.43 (s, 6 H, two CH_3CO_2–), 5.56 (d, J = 10 Hz, 1 H, H-5"), 6.25 (s, 1 H, H-3), 6.65 (d, J = 10 Hz, 1 H, H-4"), 6.90 (s, 1 H, H-8), 7.25 (d, J = 9 Hz, 2 H, H-3' and 5') and 7.84 (d, J = 9 Hz, 2 H, H-2' and 6'). All the above data agree with those described for the natural sample of carpachromene.

Reaction of 6,8 - di - C - prenyl - 5,7 - dihydroxy - 4' - methoxyflavone (5) with DDQ-formation of 5 - hydroxy - 4' - methoxy - 6 - C - prenyl - 6",6" - dimethylpyrano (2",3":7,8 flavone (22) and 5 - hydroxy - 4' - methoxy - 8 - C - prenyl - 6",6" - dimethylpyrano (2",3":7,6) flavone (21)

To a soln of 5 (0.350 g) in dry benzene (40 ml) was added DDQ (0.16 g) and the mixture refluxed for 1 hr. The product was subjected to column chromatography. Elution with benzene:light petroleum mixture (1:4) followed by benzene:light petroleum (1:1) gave two fractions A and B respectively.

Fraction A crystallised from light petroleum to afford 22 as intense yellow needles (0.1 g, m.p. 149–50°; violet ferric reaction; R_f 0.80 (solvent B), (Found: C, 74.6; H, 6.6. $C_{25}H_{26}O_5$ requires: C, 74.6; H, 6.3%); λ_{max} 263, 284 and 330 nm (4.4, 3.94 and 3.99 respectively); NMR spectrum: 1.50 (s, 6 H, $(CH_3)_2C$<), 1.70 and 1.80 (2s, 6 H, $(CH_3)_2C$=), 3.32 (d, J = 8 Hz, 2 H, Ar–CH_2–CH=), 3.85 (s, 3 H, OCH_3), 5.07–5.25 (m, 1 H, –CH=), 5.55 (d, J = 10 Hz, 1 H, H-5"), 6.50 (s, 1 H, H-3), 6.75 (d, J = 10 Hz, 1 H, H-4"), 6.95 (d, J = 9 Hz, 2 H, H-3' and 5') and 7.80 (d, J = 9 Hz, 2 H, H-2' and 6'). *m/e* 418 (50%), 403 (100%), 375 (41%), 371 (14%), 362 (28%), 349 (8%), 334 (8%), 309 (26%), 215 (28%) and 132 (25%).

Fraction B crystallised from benze-light petroleum (40–60°) mixture to yield 21 as yellow crystals (0.1 g), m.p. 115–16°; violet ferric reaction; R_f 0.75 (solvent B). (Found: C, 74.3; H, 5.9. $C_{25}H_{26}O_5$ requires: C, 74.6; H, 6.3%); λ_{max} 265, 289 and 331 (4.36, 3.72 and 3.79 respectively); NMR spectrum: 1.42 (s, 6 H, $(CH_3)_2C$<), 1.67 and 1.80 (3s, 6 H, $(CH_3)_2C$=), 3.42 (d, J = 8 Hz, 2 H, Ar–CH_2–CH=), 3.82 (s, 3 H, –OCH_3), 5.05–5.25 (m, 1 H, –CH=), 5.55 (d, J = 10 Hz, 1 H, H-5"), 6.47 (s, 1 H, H-3), 6.67 (d, J = 10 Hz, 1 H, H-4"), 6.95 (d, J = 9 Hz, 2 H, H-3' and 5') and 7.80 d, J = 9 Hz, 2 H, H-2' and 6'). *m/e* 418 (67%), 403 (100%), 371 (77%), 363 (70%), 231 (17%), 215 (33%), 203 (21%) and 132 (29%).

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