FLAVONOIDS FROM *PRUNUS PERSICA* BATSCH (PEACH BARK)*

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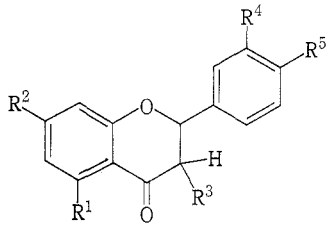
A chemical investigation of peach bark for flavonoid contents has been carried out by a number of workers.[1–4] The conflicting nature of their results and the fact that no work seems to have been done on the indigenous variety led us to reinvestigate the problem. During the progress of our work Christiansen and Boll[5] reported the isolation of a new flavanone which was characterized as 5,3′-dihydroxy-7,4′-dimethoxyflavanone (I) by synthetic and spectral evidences.



	R^1	R^2	R^3	R^4	R^5
(I)	OH	OCH_3	H	OH	OCH_3
(II)	OGl	OCH_3	H	OH	OCH_3
(III)	OH	OH	H	H	OH
(IV)	OH	OH	OH	H	OH

The present communication aims at reporting not only the details of isolation and structure determination of the free aglycones, but also of two glycosides. One of them, being a new glycoside, has been named as persiconin (5-glucosyl-3′-hydroxy-7,4′-dimethoxyflavanone) (II) and the corresponding aglycone as persicogenin (I). It may be mentioned here that a β-glucoside of hesperetin (persicoside) has already been reported[3] in peach trees, but in our hands the second glycoside was found to be a glucoside of naringenin. Shinoda and Uyeda[1] have also reported a paraffin-like substance, m.p. 280–283°, which was found to give flavanone colour reactions. They suggested that it was "probably triacontane or pentatriacontane". We were also able to obtain a colourless product from the light petroleum extract, which on purification melted at 77°. The pure product did not show the colour reaction; its absence certainly due to the removal by chromatography of free flavanone. The product, m.p. 77°, has been characterized as methyl ester of triacontanic acid[6] ("methyl mellisate") by elementary analysis, i.r. spectra, and saponification to triacontanic acid, m.p. 94° (lit.[6] 93·5°).

The present work thus describes an adequate characterization of all the flavonoidal as well as non-flavonoidal components. Further it describes the isolation

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and identification of two flavanone glycosides from the peach bark. The previous findings are either incomplete[4,5] or ambiguous.[1–3]

Experimental

All the melting points were taken on a Kofler hot microscopical stage and are corrected. Analyses were carried out by Dr K. W. Zimmermann, Australian Microanalytical Service, Melbourne. The chemical shifts, δ (p.p.m.), are relative to tetramethylsilane.

Dried and powdered bark (800 g) was extracted successively with light petroleum (40–60°), ether, and ethyl acetate in a Soxhlet. The extraction in each case was continued till the extract was almost colourless. The extracted materials had the following weight: light petroleum extract, 7·0 g; ether, 4·5 g; ethyl acetate, 3·0 g.

Light Petroleum Fraction

The yellow semi-solid mass (7·0 g) on purification from methyl alcohol gave a white waxy solid (5·0 g), m.p. 80–82°. The white solid resolved into three components by column chromatography on neutral alumina (E. Merck). Fraction A was obtained as a white solid (3·0 g), m.p. 77°, which gave no flavanone colour reactions (Found: C, 79·5; H, 13·6. Calc. for $C_{31}H_{62}O_2$: C, 79·8; H, 13·4%). I.r. (KBr disk) sharp band at 1740 cm^{-1}. It was characterized as methyl ester of triacontanic acid.[6] On saponification it gave a white solid, m.p. 94° (lit.[6] m.p. for triacontanic acid 93·5°). Fraction B (50 mg) was obtained as a colourless crystalline solid (methanol), m.p. 136–137°. It gave a phytosterol reaction. It showed no depression in melting point on admixture with an authentic sample of β-sitosterol. Fraction C (100 mg) gave flavanone colour tests and was characterized along with the ether extract.

Ether Fraction

The yellow solid (4·5 g) obtained from ether extract resolved into three components (aglycones) by column chromatography on magnesium silicate (Woelm).

5,3′-Dihydroxy-7,4′-dimethoxyflavanone (persicogenin; I).—Colourless, shining needles (1·0 g) (benzene and light petroleum), m.p. 163–164° (lit.[5] 163–164°). It gave a red coloration with magnesium and hydrochloric acid, pinkish violet colour with sodium amalgam followed by acidification, purple colour with conc. nitric acid (Found: C, 64·3; H, 5·2. Calc. for $C_{17}H_{16}O_6$: C, 64·55; H, 5·1%). I.r. (KBr disk) sharp bands at 1650 and 3435 cm^{-1}. λ_{max} (EtOH) 286, 332sh mμ. N.m.r. ($CDCl_3$): triplet 2·85 (2H) at C 3; quartet 5·35 (1H) at C 2; singlet 6·05 (2H) at C 6 and C 8; 6·9 (1H) at C 5′; 7·1 (1H) at C 2′; 7·24 (1H) at C 6′; doublet 3·85 (2OMe) at C 7 and C 4′. Diacetate, m.p. 130–132° (Found: C, 63·0; H, 5·3. Calc. for $C_{21}H_{20}O_8$: C, 63·0; H, 5·3%). N.m.r. ($CDCl_3$): triplet 2·85 (2H) at C 3; quartet 5·35 (1H) at C 2; doublet 6·42 (1H) at C 6; doublet 6·24 (1H) at C 8; 7·02 (1H) at C 5′; 7·14 (1H) at C 2′; 7·24 (1H) at C 6′; doublet 3·82 (2OMe) at C 7 and C 4′; doublet 2·32 (2AcO) at C 5 and C 3′.

Naringenin (III).—Colourless needles (alcohol and benzene), m.p. 247–248° (lit.[7] 248°). The aglycone alone and mixed with authentic naringenin was chromatographed on Whatman No. 1. filter paper using benzene–acetic acid–water (125 : 72 : 3)[8] as solvent mixture. The chromatogram on spraying with diazotized sulphanilic acid developed orange brown spots. R_F values 0·48 (lit.[8] 0·49) (Found: C, 66·55; H, 4·66. Calc. for $C_{15}H_{12}O_5$: C, 66·2; H, 4·4%). λ_{max} (EtOH) 288, 315sh mμ. N.m.r. (CD_3COCD_3): triplet 2·85 (2H) at C 3; quartet 5·41 (1H) at C 2; singlet 5·95 (2H) at C 6 and C 8; doublet 6·85 (2H) at C 5 and C 3′; doublet 7·35 (2H) at C 2′ and C 6′. Acetate, m.p. 124° (lit.[7] 126°).

Aromadendrin (IV).—Colourless aggregate of needles, m.p. 237° (lit.[9] 238–240), showed no depression in melting point when mixed with an authentic sample. The aglycone alone and mixed with authentic aromadendrin was chromatographed on Whatman No. 1 filter paper using

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acetic acid–water (60 : 40) as solvent system. The chromatogram on spraying with diazotized *p*-nitroaniline showed light brown spots, R_F 0·85 (lit.[10] 0·85). It was found identical on co-chromatography with an authentic sample on silica gel G (E. Merck) with benzene–pyridine–formic acid[11] (36 : 9 : 5) as solvent system.

It gave a red coloration with magnesium and hydrochloric acid, a cherry red colour on reduction with zinc and hydrochloric acid, and an olive green colour with alcoholic ferric chloride.

Ethyl Acetate Fraction

The yellowish brown solid (3·09 g) was purified by repeated column chromatography on magnesium silicate (Woelm) using a number of solvent systems. The last traces of accompanying free aglycones were however completely removed by column chromatography on silica gel (Light & Co.). The ethyl acetate fraction (800 mg) was separated by preparative thin-layer chromatography on silica gel G (E. Merck) using benzene–acetone (50 : 50) into two glycosidic components (A, 250 mg; B, 100 mg).

5-Glucosyl-3′-hydroxy-7,4′-dimethoxyflavanone (persiconin; II).—The glycoside (fraction A; 100 mg) on hydrolysis gave an aglycone, which crystallized as colourless needles, m.p. 163–164° (benzene–alcohol). It was characterized as 5,3′-dihydroxy-7,4′-dimethoxyflavanone (persicogenin) as detailed earlier. The hydrolysate on chromatographic examination revealed the presence of glucose only as carbohydrate moiety. The quantitative estimation of sugar by Somogyi's copper micromethod[12] confirmed the presence of one mole of sugar per mole of aglycone.

Methylation of the glycoside (100 mg) followed by hydrolysis gave an aglycone which crystallized as colourless needles, m.p. 135–136°. The partial ether thus obtained was characterized as 5-hydroxy-7,3′,4′-trimethoxyflavanone by mixed m.p. with an authentic sample.[13] I.r. (KBr disk) sharp band at 1620 cm^{-1} (characteristic of 5-hydroxy flavanones[14]).

Naringenin glucoside.—The glycoside (fraction B; 60 mg) on hydrolysis gave an aglycone, m.p. 247° (lit.[7] 248°). It was characterized as naringenin by m.p. and mixed m.p. and co-chromatography using benzene–acetic acid–water (125 : 72 : 3), R_F 0·49 (lit.[8] 0·49). The hydrolysate on chromatographic examination showed the presence of glucose as the only sugar.

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