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A NEW FLAVANONE FROM PEACH BARK

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The bark from the peach tree (Prunus persica L.) has previously been examined for flavonoids. Shinoda & Uyeda (1) have isolated naringenin (5,7,4′-trihydroxyflavanone), and Charaux & Rabaté (2) have isolated a glycoside, named persicoside, which was stated to be a monoglucoside of hesperitin (5,7,3′-trihydroxy-4′-methoxyflavanone). In 1957, Pacheco (3) by means of his colour reaction on flavanonols showed that peach bark contains aromadendrin (5,7,4′-trihydroxyflavanonol). In the present work, peach bark has been reinvestigated and among other flavonoids, we have isolated naringenin, aromadendrin, and a flavanone, the constitution of which is established as 5,3′-dihydroxy-7,4′-dimethoxyflavanone (I). The isolation procedure and structure determination of all the compounds are to be published in detail elsewhere. The compounds were isolated from an ethanolic extract of the dried bark. The alcoholic extract was separated into an ether- and a water-soluble fraction.

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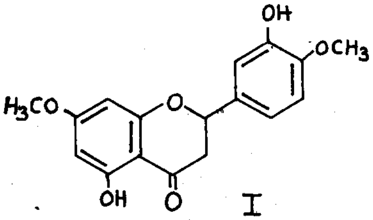


I

The ether-soluble fraction was chromatographically separated into two compounds shown to be naringenin and aromadendrin. Naringenin was identified by comparing the ultraviolet and infrared absorption with those of authentic material. Thus the work of Shinoda & Uyeda (1) has been confirmed. By comparing melting point and infrared absorption with those of authentic aromadendrin, the other compound was proved to be aromadendrin, although sligthly impure. This appears to be the first recorded isolation of aromadendrin from peach bark. The above water soluble fraction was extracted with butanol and the residue from the pooled butanol extracts was fractionated by chromatography on several columns of polyamide. A crystalline compound melting point 163-164°, was isolated.

This compound gave a red colour with magnesium and hydrochloric acid. The ultraviolet absorption (λ_{max}^{EtOH} 286 (log ε4.28), 332 (log ε3.58) nm) indicates a flavanone structure. The elementary analysis in in accord with the molecular formula $C_{17}H_{16}O_6$, corresponding to a flavanone substituted with two hydroxyl- and two methoxyl groups. The analysis of the acetyl derivative showed that two acetyl groups had been introduced.

The bathochromic shift of the ultraviolet absorption maximum in ethanolic aluminium chloride indicates a free hydroxyl group at C-5 (4) (Table I). This is confirmed by the carbonyl absorption (1635 cm^{-1}) in the infrared region (5). The insolubility in aqueous sodium carbonate and the purple colour developed on treatment of the compound with concentrated nitric acid suggest a methoxyl group at C-7 (6). The ultraviolet spectra in ethanolic sodium acetate and in ethanol were identical (Table I); this is in agreement with a methoxyl group at C-7 (4).

TABLE I

Ultraviolet Absorption Data

of 5,3′-dihydroxy-7,4′-dimethoxyflavanone

λ_{max},(log ε)

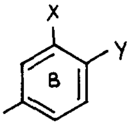
Absolute ethanol	KOH[a] in ethanol	$AlCl_3$[b] in ethanol	NaAc[c] in ethanol
286nm(4.28)	286nm(3.70)	306nm(4.56)	286nm(4.28)

a) 0.006 N KOH in absolute ethanol

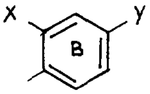
b) 0.04 M $AlCl_3$, 6 H_2O in absolute ethanol

c) Excess of fused NaAc in absolute ethanol

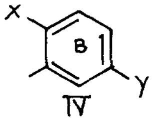
An ABX system (7) appears in the NMR spectrum (Table II, "natural") of the diacetyl derivative, corresponding to three aliphatic protons at C-2 and C-3. The two protons in the ring A show a <u>meta</u> spin-spin splitting (J=2.2 c/s) in full agreement with the suggestion that the substituents occur only in the 5- and 7-position. The signal pattern of the protons in the ring B indicates an ABC system corresponding to the following possible structures:



II



III



IV

a{ x = OCH_3
y = $OOCCH_3$

b{ x = $OOCCH_3$
y = OCH_3

TABLE II

Nuclear Magnetic Resonance Spectra of the Acetyl Derivatives of natural and synthetic 5,3'-dihydroxy-7,4'-dimethoxyflavanone

Compound	H-2	H-3$_a$ H-3$_b$	H-6	H-8	H-2'	H-5'	H-6'
natural	5.36	2.86 2.82	6.38	6.24	7.14	6.96	7.24
synthetic	5.40	2.90 2.85	6.42	6.28	7.17	6.99	7.27

The shifts δ[ppm] are relative to tetramethylsilane = 0. The spectra were recorded in deuterochloroform on a Varian HA-100 instrument.

One of these possibilities (IIb) was synthesised by selective methylation of the hydroxyl group at C-7 in hesperitin (5,7,3'-tri-hydroxy-4'-methoxyflavanone) and subsequent acetylation. The methylation was carried out with dimethylsulfate and anhydrous potassium carbonate in dry acetone according to Gupta et al. (8). The melting point, the IR spectrum, and the NMR spectrum of the synthetic 5,3'-diacetoxy-7,4'-dimethoxyflavanone are in agreement with the corresponding results for the natural compound isolated from peach bark (Table II).

Thus, peach bark contains the 7-methyl ether of hesperitin, apparantly a novel phytogenetic product.

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