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Biogenesis of Heartwood and Bark Constituents. I. A New Taxifolin Glucoside[1]

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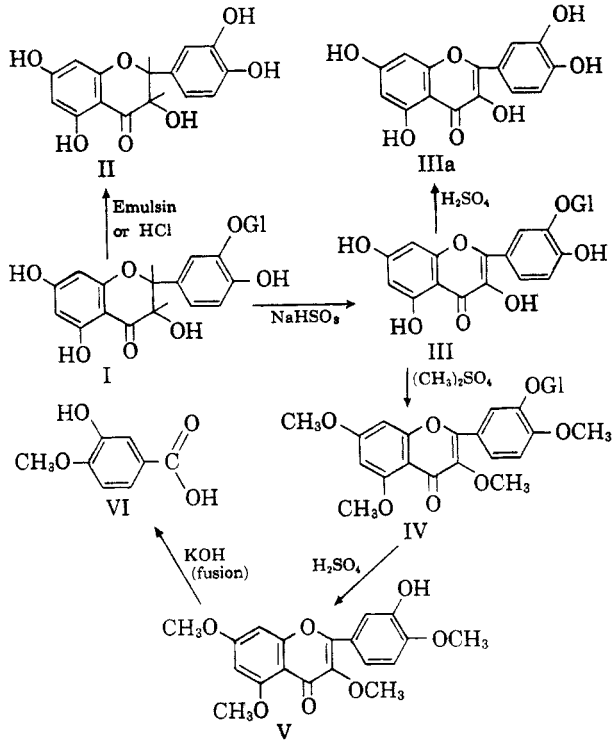
Douglas-fir needles (leaves), cambium, and sapwood have been found to contain two new glucosides, the 3′-β-glucoside of taxifolin (3,3′,4,5,7-pentahydroxyflavanone) and the 3′-β-glucoside of quercetin (3,3′,4′,5,7-pentahydroxyflavone). Taxifolin glucoside has also been found in the wood or bark of true cedar, larch, and spruce. It is suggested that taxifolin is synthesized in the leaves where it is present as the glucoside, and is then transported to the heartwood and outer bark where it is found as the aglycone.

The chemical nature and biosynthesis of heartwood and bark extractives have been the subject of much recent interest. In the case of heartwood flavonoids, Erdtman[2] has suggested that they are formed in the cambium and transported to the heartwood *via* the rays in the sapwood, while the outer bark flavonoids are synthesized in the cork cambium. Hillis[3], on the other hand, has suggested that leucoanthocyanins are synthesized in the leaves or needles and are then transported to the heartwood where they are converted to the corresponding flavones or flavanones. During the course of work on cambial constituents of various conifers, we have found a new flavonoid glucoside. The structure was determined, and from a study of the distribution of this compound in the tree, an alternate hypothesis of flavonoid biogenesis is suggested.

Determination of structure. Column chromatography of a water-soluble extract of Douglas-fir sapwood or cambium gave a white, amorphous fraction (I) which, when hydrolyzed enzymatically or with dilute acid, gave approximately one mole of glucose and one mole of (+)-taxifolin (II), a compound previously found in Douglas-fir heartwood[4,5] and outer bark.[6,7] Paper chromatography of the fraction showed it to be homogeneous, but all efforts to obtain the compound in a crystalline form were unsuccessful. Neutral and alkaline ultraviolet curves[8] were identical with those of taxifolin (II) (Fig. 1). The 7 phenolic hydroxyl group therefore was not substituted, since work on a large series of flavanones demonstrated that



glycosidation of the 7 phenolic hydroxyl in 5,7-dihydroxy flavanones causes a bathochromic shift in alkaline solution to 350 mμ.[9] Since a bathochromic shift to 314 mμ, identical with taxifolin, was observed in aluminum chloride solution, the 5 hydroxyl group was also unsubstituted. The compound gave a rose coloration with aqueous ferric chloride solution. This indicated that either the 3′ or 4′ hydroxyl group was substituted since taxifolin (II), which contains a free catechol grouping, gives a greenish black coloration with ferric chloride reagent.

Treatment with boiling sodium bisulfite[10] converted I to the corresponding quercetin glucoside (III). In contrast to I, III was readily obtainable in crystalline form. Comparison of the infrared spectrum of III (Fig. 2) with that of quercimeritrin

(1) Presented at the 132nd meeting of the American Chemical Society, Division of Cellulose Chemistry, New York, N. Y., September 9, 1957.

(2) H. Erdtman in A. Todd, *Perspectives in Organic Chemistry*, Interscience, New York (1956), pp. 453–494; Erdtman, *Proc. Royal Dublin Soc.*, **27**, 129 (1956).

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(4) J. Pew, *J. Am. Chem. Soc.*, **70**, 3031 (1948).

(5) H. M. Graham and E. F. Kurth, *Ind. Eng. Chem.*, **41**, 409 (1949).

(6) J. K. Hubbard and E. F. Kurth, *J. Am. Leather Chem. Assoc.*, **44**, 604 (1949).

(7) H. L. Hergert and E. F. Kurth, *Tappi*, **35**, 59 (1952).

(8) L. F. Maranville and O. Goldschmid, *Anal. Chem.*, **26**, 1423 (1954).

(9) O. Goldschmid, H. L. Hergert, and L. F. Maranville, unpublished work.

(10) E. F. Kurth, *Ind. Eng. Chem.*, **45**, 2096 (1953).

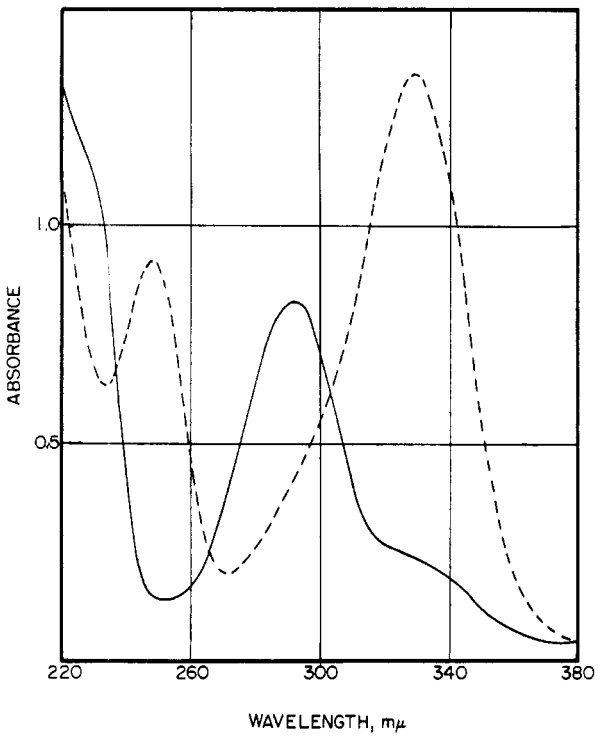

Fig. 1. Ultraviolet spectra of taxifolin-3′-glucoside, 5.68 × 10^{-5} *M*, in ethanol (——), in 0.006*N* KOH in ethanol (– – –)

(quercetin-7-glucoside) and isoquercitrin (quercetin-3-glucoside) showed non-identity. Comparison of the properties of III with those reported for spiraeoside[11] demonstrated that III was not quercetin-4′-glucoside. Comparison of the neutral, alkaline, alkaline-borate[12] and aluminum chloride[13] ultraviolet curves of III (Fig. 3) showed slight deviations from those of quercetin (IIIa) but were nearly identical with those of kaempferol (3,4′,5,7-tetrahydroxyflavone). This indicated that III does not have a free phenolic hydroxyl group in the 3′ position, and III was therefore indicated to be quercetin-3′-glucoside.

Methylation of III and subsequent hydrolysis gave a crystalline quercetin tetramethyl ether (V), the properties of which corresponded to those reported for synthetic quercetin-3,4′,5,7-tetramethyl ether[14,15]. Comparison of the neutral and alkaline

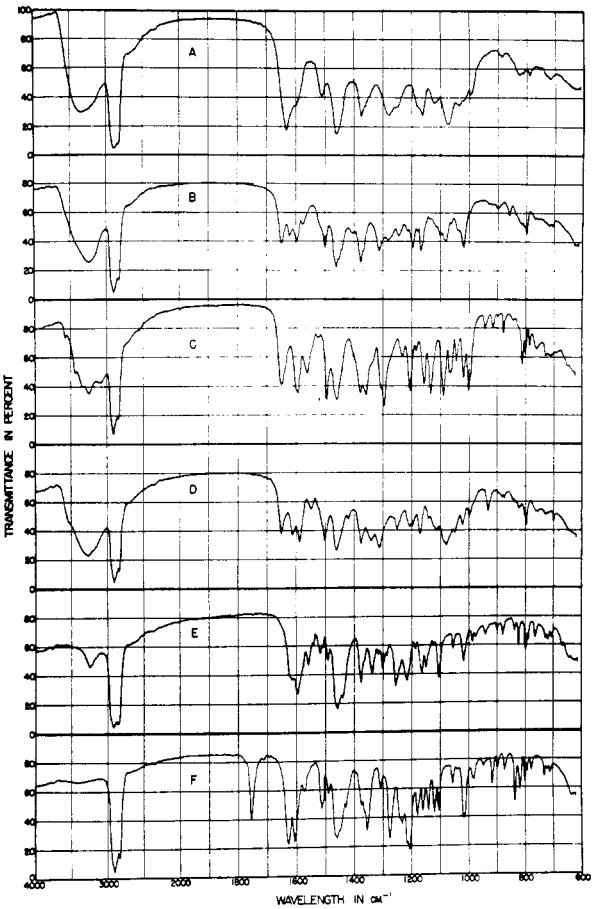

Fig. 2. Infrared spectra (paraffin mulls) of A. Taxifolin-3′-glucoside, B. quercetin-3′-glucoside, C. quercetin-3-glucoside, D. quercetin-7-glucoside, E. 3,4′,5,7-tetra-*O*-methyl quercetin, and F. 3,4′,5,7-tetra-*O*-methyl quercetin acetate

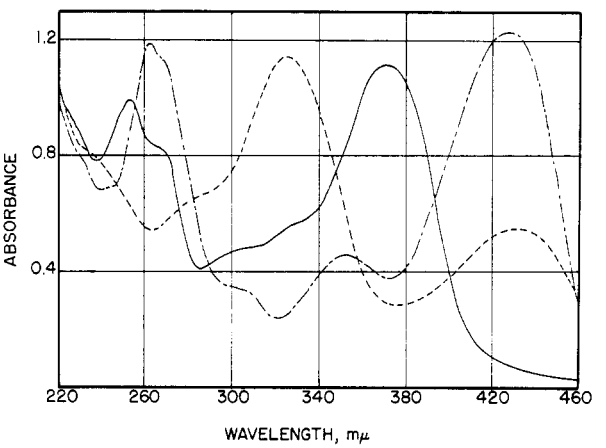

Fig. 3. Ultraviolet spectra of quercetin-3′-glucoside, 5.12 × 10^{-5} *M*, in ethanol (———), in 0.002*M* sodium ethoxide (– – – –), in 0.04*M* aluminum chloride in ethanol (— – —)

ultraviolet spectra of V with those of a series of partially methylated flavones[16] indicated that the free phenolic hydroxyl group was in the 3′ position. In order to confirm further the structure of V, the

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(12) T. Swain, *Chem. & Ind. (London)*, 1480 (1954).

(13) J. B. Harborne, *Chem. & Ind. (London)*, 1142 (1954).

(14) F. E. King, T. J. King, and K. Sellars, *J. Chem. Soc.*, 92 (1952).

(15) N. Narasimhachari, S. Narayanaswami, and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **37A**, 104 (1953).

(16) C. G. Nordström and T. Swain, *J. Chem. Soc.*, 2764 (1953).

acetate derivative of V was submitted to an alkaline hydrolysis and isovanillic acid was identified as a degradation product. These experiments showed that III was quercetin-3′-glucoside and that I was taxifolin-3′,β,D-glucoside.

Two-dimensional paper chromatography of the sapwood and cambial extracts of Douglas-fir showed that in addition to I, a flavone glucoside was present. Comparison of R_f values indicated it to be identical with synthetic quercetin-3′-glucoside (III). As far as may be ascertained, neither flavanone or flavone glucosides have been previously reported as conifer wood constituents. Flavonoid glucosides have been reported from conifer leaves, however. Quercitrin (quercetin-3-rhamnoside) has been obtained from sawara cypress,[17] and quercimeritrin was found in cryptomeria.[18] A taxifolin glucoside of undetermined composition has been reported to be present in hinoki cypress leaves[19] and the wood[20] of a Japanese plum.

Distribution of taxifolin-3′-glucoside. Two-dimensional chromatograms were made of extracts from various parts of a Douglas-fir tree. Results are shown in Table I. The presence of taxifolin-3′-glucoside and quercetin-3′-glucoside and the absence of flavanone or flavone aglycones in the needles, inner bark, cambium, and sapwood suggest that quercetin and taxifolin are synthesized and glycosylated in the needles (leaves) and are then transported down the inner bark. They are then transported transversely *via* the rays to the heartwood and outer bark, the sugar being removed at or near the sapwood-heartwood and inner-outer bark boundaries to form the aglucone.

In order to test the applicability of this hypothesis to other coniferous genera, extracts were made of sapwood, heartwood, and/or bark of various representative species. Chromatographic results are shown in Table II.

TABLE I

DISTRIBUTION OF FLAVONOIDS IN DOUGLAS-FIR

Source	Compound			
	Taxifolin-3′-glucoside	Taxifolin	Quercetin-3′-glucoside	Quercetin
Needles[a]	+	−	Tr	−
Branches[a]	+	−	Tr	−
Inner bark	Tr	−	Tr	−
Cambium	+	−	Tr	−
Sapwood[b]	+	−	Tr	−
Sapwood[c]	+	Tr	Tr	−
Heartwood	−	+	−	Tr
Outer bark	Tr	+	−	Tr
R_f in 2% acetic acid	.47	.29	.01	.00
R_f in BuOH-HAc-H_2O (4:1:5)	.54	.81	.38	.71

[a] Additional flavonol glycosides also present. [b] Adjacent to cambium. [c] Adjacent to heartwood. + = compound present, Tr = trace, − = absent.

TABLE II

DISTRIBUTION OF TAXIFOLIN AND TAXIFOLIN-3′-GLUCOSIDE AMONG CONIFERS

Species	Part of Tree	Compound	
		Taxifolin-3′-glucoside	Taxifolin
Atlas cedar	Sapwood	+	−
	Heartwood	−	+
	Bark	Tr	+
Western larch	Needles[a]	+	−
	Bark	Tr	+
	Sapwood[b]	+	−
	Heartwood[b]	−	+
Sitka spruce	Needles[a]	+	−
	Inner bark	+	−
	Outer bark	Tr	+
	Sapwood	+	−
	Heartwood	−	+
Western red cedar	Outer bark	Tr	+
Bald cypress	Outer bark	−	−
Western hemlock	Needles[a]	Tr	−
	Bark	−	−
	Cambium	−	−
	Sapwood	−	−
	Heartwood	−	−
Pacific silver fir	Needles[a]	Tr	−
	Bark	−	−
	Sapwood	−	−
	Heartwood	−	−

[a] Additional flavonol glycosides also present. [b] Aromadendrin present.

All coniferous species thus far examined, when found to contain taxifolin in the heartwood or outer bark, have also been found to contain taxifolin glucoside. Hemlock and true fir, which do not appear to contain taxifolin in the wood or bark, have only trace amounts of taxifolin glucoside in the needles. It is recognized that in order to establish definitely the biogenetic origin of the heartwood flavonoids, the radioactive tracer technique will have to be used, but determination of the nature of the flavonoid constituents in different species appears to be a necessary preliminary to such work.

The present paper is concerned only with those species which have relatively simple flavonoid systems. Taxifolin glucoside has also been found in the pine genus, which contains a considerably more complex system. This will be discussed in a subsequent paper.[21] Preliminary work on the needle extracts of Douglas-fir and western hemlock in-

(17) M. Hasegawa, H. Nakamura, and S. Tsuruno, *J. Jap. Forestry Soc.*, **37**, 488 (1955).

(18) T. Kondo and H. Ito, *J. Agr. Chem. Soc., Japan*, **28**, 290 (1954); T. Kondo and H. Furuzawa, *J. Jap. Forestry Soc.*, **36**, 190 (1954).

(19) T. Kariyone and Y. Fukui, *J. Pharm. Soc., Japan*, **76**, 343 (1956).

(20) M. Hasegawa, *J. Jap. Forestry Soc.*, **38**, 107 (1956).

(21) H. L. Hergert, Paper II of this series.

dicates the presence of other flavonol glycosides which, on the basis of chromatography and hydrolysis products, have not been previously described in the literature.

EXPERIMENTAL[22]

Preparation of extractives. Cambial material was carefully scraped in September, 1955, and June, 1956, from approximately 40-year old Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] trees, growing in the vicinity of Shelton, Wash. The cambial material was immediately placed in methanol and the methanol extract worked up within a day of collection. An individual 60-year old Douglas-fir tree was felled and samples of the heartwood, sapwood adjacent to the heartwood and to the cambium, inner bark, outer bark, one-year old branches, and needles were procured. A large sample of sapwood was prepared by peeling six- to ten-year old branches of several trees. Needles were collected from trees of varying age at monthly intervals during late spring and summer. As soon as each wood or bark sample was procured, it was ground in a Wiley mill to pass a 20-mesh sieve. It was then exhaustively extracted with methanol at 25°. The methanol extracts were concentrated to 10–20% solids content and retained for chromatography or further separation.

Wood, bark, and/or needle samples were procured and extracted from the following coniferous species: Sitka spruce [*Picea sitchensis* (Bong.) Corr], 8, 150, and 450 years, Mason County, Wash.; western hemlock [*Tsuga heterophylla* (Raf.) Sarg.], 75 to 150 years, Mason County, Wash.; western red cedar (*Thuja plicata* Donn), 125 years, near Hoquiam, Wash.; western larch (*Larix occidentalis* Nutt.), branch 12 years of age, Seattle, Wash.; Pacific silver fir [*Abies amabilis* (Dougl.) Forbes], 50 to 75 years, north Vancouver Island, B. C.; grand fir [*Abies grandis* (Dougl.) Lindl.], 125 years, Mason County, Wash.; Atlas cedar (*Cedrus atlantica*, probably var. *glauca* Carriere), 40 years, Shelton, Wash.; and bald cypress (*Taxodium distichum*), 75 to 200 years, southeastern Ga.

Chromatography. The total methanol extract (or in the case of samples which contained tannin, the methyl ethyl ketone-soluble fraction obtained by liquid-liquid extraction of the water-soluble portion of the original methanol extract) was chromatographed two-dimensionally[23] on prewashed Whatman No. 1 paper with the organic phase of butanol–acetic acid–water (4:1:5) and 2% acetic acid by the descending method. Chromatograms were dried, examined under ultraviolet light before and after fuming with ammonia, and then sprayed with 1% ferric chloride–potassium ferricyanide,[24] diazotized sulfanilic acid,[25] bis-diazotized dianisidine,[26] and cinnamaldehyde-HCl.[21]

Taxifolin-3′-glucoside (I). Douglas-fir sapwood (1.0 kg., o.d. basis) was suspended in 20 l. of acetone-methanol (1:5) for 24 hr. at 25° in a covered stainless steel can. The extract was drained, filtered, and evaporated to 100 cc. at 20° in a natural circulation, borosilicate glass evaporator. The recovered solvent was used to make two additional extractions of the wood. The combined extracts were evaporated to a small volume, the methanol replaced with water, and the aqueous extract thoroughly liquid-liquid extracted with ether. The ether extract, consisting of waxes, fats, etc., was discarded. The aqueous extract was treated with one gram of decolorizing carbon, filtered, evaporated *in vacuo* to 25 cc., and applied to a Gryksbo (rolled filter paper) chromatographic column[27] which had been prewashed with distilled water. The column was then eluted with distilled water and 20-cc. fractions were collected. After 2875 cc. of eluent had been collected, 630 cc. of taxifolin-3′-glucoside solution, readily detected by a rose coloration with 1% ferric chloride reagent, was obtained. This fraction was evaporated *in vacuo* and then freeze-dried to yield a white powder, m.p. 203–205°, $[\alpha]_D^{25}$ −23° (water, c. 0.3). Yield, 375 mg., 0.04% based on the oven-dry weight of sapwood. The product was very soluble in water, soluble in methanol and ethanol, insoluble in dry acetone, ethyl acetate, and ether. Attempts to crystallize taxifolin-3′-glucoside from a variety of solvents were unsuccessful.

Anal. Calcd. for $C_{21}H_{22}O_{12}\cdot 2H_2O$: C, 50.20; H, 5.22. Found: C, 49.53; H, 5.57.

The ethanolic solution of the product gave a cerise coloration upon treatment with powdered zinc and hydrochloric acid.[4] The neutral and alkaline ultraviolet spectra are presented in Fig. 1 and the infrared spectrum in Fig. 2A.

Taxifolin-3′-glucoside (75 mg.) in 20 cc. water was mixed with 5 cc. of 5% emulsin (β-glucosidase) solution and allowed to stand 48 hr. at 25°. The aqueous solution was then thoroughly extracted with ether. The ether extract was evaporated to dryness, taken up in 5 cc. hot water, filtered, and allowed to crystallize. White crystals, m.p. 240–241°, undepressed mixed melting point with *d*-taxifolin from Douglas-fir heartwood, 240–242°, were obtained. The infrared spectrum was identical with authentic *d*-taxifolin.[28]

Taxifolin-3′-glucoside [0.0283 mmole (13.7 mg.)], was dissolved in 10 ml. of 1*N* sulfuric acid and refluxed for 4 hr. The cooled solution was exhaustively extracted with ether to give 0.024 mmole (7.36 mg.) taxifolin. The ether-extracted aqueous fraction was neutralized with barium carbonate, filtered, and shaken with IR 120 (Rohm & Haas Co.) resin to remove barium ions. The solution was concentrated and the sugar content determined by a paper chromatographic method similar to that of McCready and McComb.[29] The yield was 0.024 mmole (4.36 mg.) glucose.

Quercetin-3′-glucoside (III). Taxifolin-3′-glucoside (0.4 g.) was dissolved in 100 cc. of aqueous 15% sodium bisulfite solution. The mixture was refluxed for 3 hr., allowed to stand 1 hr., and filtered. The yellow precipitate was recrystallized once from hot water and twice from acetone-water (1:3) to give 0.3 g. of yellow needles, m.p. 216° (softens 196°).

Anal. Calcd. for $C_{21}H_{21}O_{12}\cdot 1.5H_2O$: C, 50.71; H, 4.66. Found: C, 51.03; H, 4.34.

Two-dimensional chromatography gave a single spot, yellow under ultraviolet light, purple-brown with bis-diazotized dianisidine. A spot of identical R_f and color reaction was observed on chromatograms of Douglas-fir cambial and sapwood extracts. Quercetin-3′-glucoside (0.1 g.) was hydrolyzed in 20 cc. of 5% sulfuric acid for 6 hr. Ether extraction of the aqueous hydrolysate and subsequent recrystallization from 30% ethanol gave 40 mg. of yellow crystals, m.p. 308–310°, mixed melting point with authentic quercetin undepressed.

Quercetin-3′-glucoside (250 mg.) and anhydrous potassium carbonate (4 g.) were suspended in 25 cc. dry acetone. The mixture was refluxed for 2.5 hr. during which time 2.5 cc.

(22) All melting points are corrected; microanalyses by Weiler and Strauss, Oxford, England; infrared spectra were obtained as Nujol mulls on a Perkin-Elmer Model 21 double-beam spectrophotometer; ultraviolet spectra were determined on a Cary Model 11 recording spectrophotometer.

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(25) M. T. Hanke and K. K. Koessler, *J. Biol. Chem.*, **50**, 235 (1922).

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TABLE III

ULTRAVIOLET ABSORPTION SPECTRA

Compound	λ_{max}, mμ, and (Log ε) 95% Ethanol			Alkaline[a]-EtOH			$AlCl_3$[b]-EtOH			$NaOEt-H_3BO_3$-EtOH[12]		
Taxifolin-3′-glucoside	227 (4.35)	292 (4.19)	329 (3.65)	249 (4.24)	329 (4.42)		224 (4.19)	314 (3.96)	377 (3.17)			
Taxifolin	229 (4.39)	291 (4.27)	326 (3.35)	246 (4.04)	329 (4.38)		224 (4.43)	314 (4.31)	380 (3.52)			
Isosakuranin	227 (4.40)	284 (4.20)	332 (3.46)	242 (4.16)	336 (3.96)	350 (4.13)	224 (4.50)	307 (4.26)	380 (3.52)			
Verecundin	224 (4.28)	286 (4.17)		254 (3.88)	331 (4.41)		No shift					
Quercetin-3′-glucoside	253 (4.29)	325 (4.03)	370 (4.34)	240 (4.19)	325 (4.35)	432 (4.03)	262 (4.36)	352 (3.95)	428 (4.38)	280 (4.12)	325 (4.26)	423 (4.25)
Kaempferol	268 (4.19)	324 (3.99)	368 (4.26)	246 (4.11)	325 (4.27)	430 (3.93)	270 (4.26)	350 (3.92)	428 (4.32)	280 (4.05)	325 (4.19)	419 (4.27)
Quercetin	256 (4.32)	301 (3.89)	373 (4.32)	247 (4.08)	334 (4.27)	420 (3.86)	268 (4.33)	360 (3.88)	431 (4.37)	276 (4.18)	330 (4.05)	410 (4.23)
3,4′,5,7-tetra-*O*-methyl quercetin	251 (4.32)	264	341 (4.28)	260 (4.36)	333 (4.10)	380 (3.98)						
4′,5,7-tri-*O*-methyl luteolin[16]	245	—	334	259	—	380						

[a] 0.006*N* KOH for flavanones, 0.002*N* NaOEt for flavones. [b] 0.04*M*. ~ Shoulder or inflection.

of dimethyl sulfate was added in 0.5 cc. portions. The acetone was evaporated at room temperature and the mixture dissolved in 50 cc. water. After standing 24 hr., a white precipitate was filtered off and recrystallized twice from 50% ethanol to yield, 150 mg. of methylated quercetin-3′-glucoside, m.p. 219–220° (sinters 145–150°). The white crystals gave no coloration with ferric chloride reagent and they were insoluble in 5% aqueous sodium hydroxide. This indicated that all phenolic groups had been methylated.

3,4′,5,7-tetra-O-methyl quercetin (V). Methylated quercetin-3′-glucoside (100 mg.) was dissolved in a mixture of 50 cc. 50% ethanol and 1 cc. concentrated sulfuric acid. After refluxing for 2 hr., the ethanol was removed by evaporation and the mixture set aside to crystallize. After two recrystallizations from 80% ethanol, cream colored needles of V, m.p. 224–225°, were obtained (lit., for V, 223–224°,[15] 220–222°,[14] while 3,3′,5,7-tetra-*O*-methyl quercetin has m.p., 200–201°,[30] 202–203°[11]). A yellow coloration was imparted to alkaline solution by the crystalline V.

Anal. Calcd. for $C_{19}H_{18}O_7$: C, 63.66; H, 5.07. Found: C, 64.17; H, 4.94.

The acetate derivative of V was prepared by dissolving V (20 mg.) in 2 cc. acetic anhydride and 0.3 cc. pyridine. After standing 24 hr., the mixture was poured into water and the insoluble precipitate recrystallized twice from methanol to yield 16 mg. of small white needles, m.p. 215–216°. The infrared spectrum (Fig. 2F) showed an acetoxy carbonyl absorption at 1760 cm.$^{-1}$ and a conjugated carbonyl band at 1625 cm.$^{-1}$, which is consistent with the structure, 3′-acetoxy-3,4′,5,7-tetramethoxyflavone.[31]

Degradation of acetate of V. The acetate of V (10 mg.) was dissolved in a mixture of 4.5 cc. ethanol, 1.5 cc. water, and 20 mg. sodium hydroxide. This was heated with shaking for 2 hr. at 175° in a semimicro stainless steel bomb fitted with a Teflon gasket. The degradation mixture was acidified, the ethanol removed by evaporation and the resultant aqueous mixture extracted with ether. Chromatography of the ether extract with butanol saturated with 2% ammonium hydroxide[32] by the descending method gave two spots: R_f 0.06, isovanillic acid, red when sprayed with bis-diazotized benzidine (vanillic acid has R_f 0.09, gives brown color with this spray); R_f 0.90, α,2,4-trimethoxy, 6-hydroxy acetophenone, light brown when sprayed with 2,4-dinitrophenylhydrazine, and yellow with diazotized sulfanilic acid (identical with the same product derived through a similar degradation of penta-*O*-methylquercetin). Repetition of the degradation with less alkali and for only 30 min. gave an additional chromatographic spot, R_f 0.81, isovanillin, tan with bis-diazotized benzidine, and orange-brown with 2,4-dinitrophenylhydrazine spray (vanillin has R_f 0.46 and slightly different colors with the same spray).

The ether extract from the degradation was evaporated to dryness and taken up in 5 cc. of warm water. The acetophenone derivative was relatively insoluble in water and could be filtered out. Upon cooling the filtrate, 1.5 mg. of white crystals were obtained, m.p. 248° (after recrystallization), mixed melting point with authentic isovanillic acid, 248–249°.

Chromatography of needle extract. Two-dimensional chromatograms of the methyl ethyl ketone–water soluble fraction from Douglas-fir needles showed a spot corresponding to (+)-catechin (R_f in butanol–acetic acid and 2% acetic acid, respectively) at 0.56–0.44, orange-brown with cinnamaldehyde–hydrochloric acid spray; flavonol glucoside spots (yellow when fumed with ammonia under ultraviolet light) at 0.31–0.10, 0.44–0.16, 0.58–0.20, 0.24–0.25, 0.30–0.39, 0.41–0.39, and 0.68–0.12; and the taxifolin-3′ glucoside spot at 0.54–0.47. The first three of the flavonol glucoside spots, spots for additional different flavonol glycosides, and spots of catechin, gallocatechin, and taxifolin-3′-glucoside have also been identified on chromatograms of western hemlock and larch needle extracts.

Absorption spectra. The absorption spectra of compounds prepared during the course of this study are recorded in Table III. We wish to thank Dr. Simon Wender for a gift of isoquercitrin, Dr. T. Kondo for quercimeritrin, and Dr. M. Hasegawa for verecundin and isosakuranin.

SHELTON, WASH.

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