ether and the combined ethereal extracts were washed three times with 50 ml portions of water. The ether solution was dried over anhydrous $MgSO_4$ and concentrated to dryness. The crude consisted of solid and an oil. Approximately 10 g of solid (**2**) were filtered off and 16 g of oil (**3**) remained. The oil was distilled at 114–116 °C/0.1 mm and the solid was recrystallized from ethanol and had m.p. 127–127.5 °C (lit. (1), m.p. 129.5–130.5°). A vapor-phase chromatography analysis employing an F and M model 810 equipped with a 3 ft silicon gum rubber column indicated that the crude mixture had at least two other minor components representing less than 5% of the total besides **2** and **3**.

Anal. Calcd. for **3**, $C_{16}H_{10}ClF_4P$: C, 55.76; H, 2.90; Cl, 10.28; P, 8.99. Found: C, 55.36; H, 3.14; Cl, 10.41; P, 8.78.

Infrared spectrum (neat): some of the more significant peaks are 3060w, 1575m, 1480m, 1320s, 1120vs, 1070w, 1030w, 1000m, 860s, 835s, 745s, 693s. Nuclear magnetic resonance: the phosphorus spectrum shows only one peak at +25.1 p.p.m., which is in agreement for a tertiary phosphine (10).

Anal. Calcd. for **2**, $C_{28}H_{20}P_2F_4$: C, 68.03; H, 4.04; P, 12.54. Found: C, 68.29; H, 4.38; P, 12.71.

Infrared spectrum (mull): some of the more significant peaks are 1595w, 1435m, 1375w, 1295s, 1220s, 1155s, 1085s, 1065w, 1025w, 1000w, 830m, 822m, 758m, 740s, 730w, 725m, 694s. Nuclear magnetic resonance: the phosphorus spectrum shows only one peak at 22.7 p.p.m. which is in agreement for a tertiary phosphine (10). A sample of **2** was obtained from Professor W. R. Cullen (1) and it was shown by i.r., ^{31}P n.m.r., and a mixture melting point, to be identical to that obtained in this work.

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7-*O*-β-D-Glucosyl-3′,4′,5-trihydroxy-6-methyl flavanone—a new *C*-methyl flavanone glycoside from Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] roots

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A new *C*-methyl flavanone, 7-*O*-β-D-glucosyl-3′,4′,5-trihydroxy-6-methyl flavanone, has been obtained from healthy Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] root bark in a high yield of 2.6%. Its structure was elucidated by high resolution and mass spectrometry together with a variety of chemical and physical tests and confirmed by synthesis of its methylated aglycone. Pathological testing of this new glucoside against *Poria weirii* Murr. is being undertaken.

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The first new *C*-methyl flavanone, poriol, to be discovered in Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] roots has been described in a previous paper (1). In contrast to poriol, which was obtained in low yield (0.2%) from diseased (*Poria weirii* Murr.) Douglas-fir root bark, the new *C*-methyl flavanone glucoside (**1**) was obtained in high yield (2.6%) from healthy Douglas-fir root bark. The structure of this new *C*-methyl flavanone glucoside (**1**) is proposed as 7-*O*-β-D-glucosyl-3′,4′,5-trihydroxy-6-methyl flavanone.

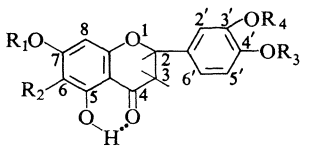
Flavanone glucoside (**1**) crystallized from an ethyl acetate extract of healthy Douglas-fir root bark. This bark had been previously extracted

(soxhlet) with chloroform to remove interfering substances. White crystals were obtained, melting at 228.5 °C (Mettler FP 1). After recrystallization from aqueous methanol, the melting point was raised to 255.1 °C.

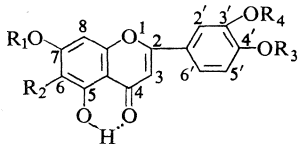
Flavanone glucoside (**1**) gave positive phenolic tests with Barton's reagent (2) (blue) and diazotized sulfanilic acid (3) (yellow). The 3-hydroxy flavanone test (4) developed for thin-layer chromatography (t.l.c.) proved negative, but the Shinoda test (5) was positive (violet). Its infrared (i.r.) spectrum was similar to flavanone glucosides such as hesperedin. Principal absorption peaks were ν(KBr) 530 (w), 545 (w), 565 (w), 615 (w), 625 (w), 690 (m), 720 (m), 740 (m), 760 (m), 785 (w), 815 (s), 865 (m), 880 (m), 890 (m), 915 (s), 960 (s), 1030 (m), 1070 (m), 1080 (m), 1130 (m), 1170 (s), 1190 (m), 1240 (m), 1290 (s), 1320–1350 (br, m), 1435 (m), 1450 (m), 1490 (m), 1540 (m), 1580 (m), 1605 (w), 1635 (s), 2920 (m), 2940 (m), 2960 (w), 3000–3560 (br, s).

Its ultraviolet (u.v.) spectrum was typical of a substituted flavanone λ_{max} 288 (log ε 4.31) λ_{min} 251 mμ (isopropanol).

The 100 Mc.p.s. nuclear magnetic resonance (n.m.r.) spectrum of its acetate (**2**) in deuteriochloroform showed clearly that it was a monoglucoside with 4 free aromatic protons. The AB part of the expected ABX absorption pattern of ring C protons was easily discernable, centered at 7.2 τ. Mold hydrolysis of **1** (300 mg) with a mixture of hydrochloric – acetic acid (0.2 ml concentrated hydrochloric acid, 5 ml of glacial acetic acid) for 30 min at 100 °C gave two main fragments, glucose and aglycone (**3**) which were identified by t.l.c. The first preparations of the glycosides (**1**) after hydrolysis gave, in addition to glucose, a small quantity of rhamnose. Recrystallization of the glucoside (**1**) from ethanol (trace of water) resulted in only glucose and aglycone (**4**) being formed. It has not been determined whether the rhamnose was present as a free sugar impurity or whether a small quantity of rhamnoside co-crystallized with the glucoside. Lack of an extra methyl group (required for the C-6 position of rhamnose) in the n.m.r. spectrum of the glycoside acetate (**2**) precluded the possibility of a rutinoside. High-resolution nuclear magnetic resonance of the methylated aglycone (**4**) enabled probable assignments to be made as follows: τ (deuteriochloroform): 2.06 (1H, singlet, hindered hydroxyl group C-5), 3.10 (3H, multiplet, aromatic protons ring B), 3.95 (1H, singlet, aromatic proton C-8), 4.60, 4.73 (1H, doublets, X part of ABX, J_{BX} = 3.5 c.p.s. proton C-2), 6.10 (3H, singlet, methoxyl C-3′ or C-4′), 6.13 (3H, singlet, methoxyl C-3′ or C-4′), 6.20 (3H, singlet, methoxyl C-7), 7.07 (2H, mulitplet, AB part of ABX, J_{AB} = 17.5 c.p.s., J_{AX} = 12.5 c.p.s., C-3), 8.01 (3H, singlet, methyl, C-6).



1 R_1 = glucose, R_2 = CH_3, R_3 = R_4 = H
2 R_1 = glucose acetate, R_2 = CH_3, R_3 = R_4 = acetate
3 R_1 = R_3 = R_4 = H, R_2 = CH_3
4 R_1 = R_2 = R_3 = R_4 = CH_3
6 R_1 = R_2 = R_3 = H, R_4 = CH_3



5 R_1 = R_2 = R_3 = R_4 = CH_3

The high value (12.5 c.p.s.) for the coupling constant J_{AX} is indicative of an axial–axial coupling only. Therefore, the C-2 hydrogen is axial and ring B is equatorial (6).

The mass spectrum of **4** showed a strong parent ion peak at *m/e* 330 (100) and 3 main fragments at *m/e* 164 (99), 151 (86), and 133 (43). The abundance of the 164 fragment indicates great stability of 3,4-dimethoxystyrene arising from the expected cleavage between C-1 and the heterocyclic oxygen and between C-3 and C-4. The fragments are consistent with structure **4**.

Since the n.m.r. spectrum of **4** had shown the presence of three methoxyl groups and color tests (7) indicated that compound **1** had vicinal phenolic hydroxyl groups, it must be concluded that the glucoside was formed at the non-vicinal hydroxyl group. Subsequent experiments showed that this hydroxyl group was on C-7 and hence the sugar moiety was associated with ring A at C-7. The successful hydrolysis of compound **1** by emulsin showed that it was a β-glucoside.

Final proof of structure was obtained in two ways. It was shown that dehydrogenation of the methylated aglycone (**4**) with iodine and glacial

acetic acid (30 mg of **4** was refluxed for 2 h with 30 mg of iodine in 5 ml of glacial acetic acid) followed by purification on t.l.c. (silica gel, carbon tetrachloride – methanol (7:1) R_f 0.61) resulted in the known compound 6-methyl-luteolin, 7,3′,4′-trimethylether (**5**) melting at 197.6 °C. It was also shown that nuclear methylation of hesperetin (**6**) at C-6 with methyl iodide and sodium methoxide (8) resulted in the methylated aglycone (**4**). This result was confirmed by quantitative i.r. comparison and mixture melting point 176.8 °C. Thus the structure of the new *C*-methyl flavanone glucoside is 7-*O*-β-D-glucosyl-3′,4′,5-trihydroxy-6-methyl flavanone. Pathological testing of this glucoside (**1**) against *Poria weirii* is currently being undertaken by Dr. G. W. Wallis at the Forest Research Laboratory, Victoria, British Columbia.

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