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GLYCOSIDES FROM *PINUS CONTORTA* NEEDLES*

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Key Word Index—*Pinus contorta*; Pinaceae; lodgepole pine needles; monolignol glucosides; zingerone; rheosmin; chavicol; dihydro-*p*-coumaryl alcohol.

Abstract—The β-D-glucopyranosides of zingerone, rheosmin acetoxydihydro-*p*-coumaryl alcohol, chavicol, benzoic acid and 2(or 4)-hydroxy-4(or 2)-methoxyprop-1-ene were isolated from the water soluble fraction of *Pinus contorta* needles, in addition to a dilignol-L-rhannopyranoside.

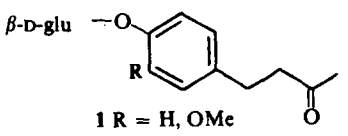
INTRODUCTION

Research into host preference has shown a variation in susceptibility to the European sawfly (*Neodiprion sertifer*) between different provenances of *Pinus contorta* [1]. Concurrent with biological studies on the behaviour pattern of the sawfly larvae, a further investigation of lodgepole pine needles (Coastal) has resulted in the identification of a further 7 glycosides in the water soluble fraction; this paper describes the structure elucidation of these compounds. In a previous paper [2] we recorded the isolation of 4 monolignol glucosides, chavicol 4-*O*-β-L-arabinofuranosyl-(1→6)-β-D-glucopyranoside, the known 4'-*O*-β-D-glucopyranoside of 2,3-dihydro-7-hydroxy-2-(4'hydroxy-3'-methoxyphenyl)-3-hydroxymethyl-5-benzofuranpropanol and shikimic acid.

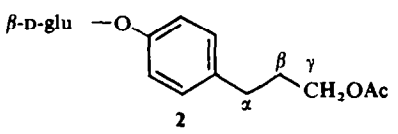
RESULTS AND DISCUSSION

The isolation and purification procedures for the compounds, tentatively numbered compounds 8–14, is described in detail in the Experimental section and only such data relevant to the structural assignments will be referred to in the subsequent discussion.

A phenylbutan-2-one structure is given to compounds 8 and 9. Their relationship was evident from their chemical behaviour and analysis of their spectral data. Both compounds have OH and carbonyl absorptions in their IR spectra. Based on chemical shift values in the PMR spectra, the carbonyl group was placed adjacent to a Me group (δ 2.2 (COMe)) and separated from the aromatic moiety by two methylene groups (δ 2.86 (4H, —CH_2—)). Hydrolysis of compounds 8 and 9 with emulsin afforded glucose but different aglycones. The aglycone from compound 8 proved to be zingerone [3] and that from 9 rheosmin [4]. The structures of the aglycones were confirmed by comparison (PMR, TLC) with authentic samples. The peracetates of the glucosides (1, R = H, OMe) had a sugar to aglycone ratio of 1:1 and PMR confirmed the pyranoside form of the sugar. A negative molecular rotation (−117.8°) for compound 8 (1, R = OMe) agrees with the assignment of a β-linkage to the glucose. Consequently, compound 8 is zingerone 4-*O*-β-D-glucopyranoside. The PMR spectrum of glucoside (1, R = H) shows an anomeric proton signal at δ 4.9 (*m*, w(h/2) = 10 Hz) characteristic of a β-configuration for the sugar unit. The compound is, therefore, rheosmin 4-*O*-β-D-glucopyranoside. This glycoside resembles that isolated from rhizomes of *Rhei palmati* [5].



1 R = H, OMe



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The co-occurrence of 4-hydroxy- and 4-hydroxy-3-methoxy- oxygenation patterns in the glucosides 8 and 9 indicates that the C_6–C_3 moiety is derived from the shikimic-prephenic pathway. The additional carbon in the aglycones, zingerone and rheosmin is likely to arise by condensation of cinnamate or dihydrocinnamate with malonate followed by decarboxylation. By analogy with the biosynthesis of [6]-gingerol [6] the biosynthetic route to zingerone would be phe → *p*-coumaric acid → ferulic acid → dihydroferulic acid → $ArCH_2CH_2CO.CH_2CO_2SCoA$ → zingerone.

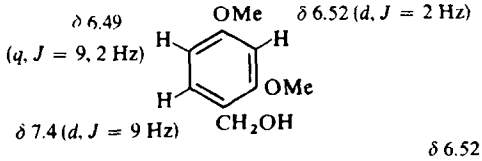
The structure γ-*O*-acetyl-dihydrocoumaryl alcohol 4-*O*-β-D-glucopyranoside (2) is assigned to compound 10 because alkaline hydrolysis gave the known dihydrocoumaryl alcohol 4-*O*-β-D-glucopyranoside [2] whilst hydrolysis with emulsin afforded D-glucose and γ-*O*-acetyl-dihydro-*p*-coumaryl alcohol in a 1:1 ratio. The β-D-glucopyranoside configuration is based on data from the PMR spectra of 2 and that of its peracetate.

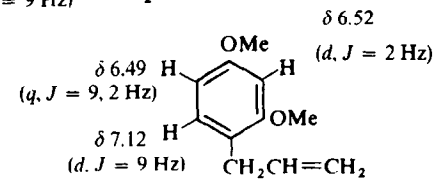
The optically active compound 11 is an amorphous solid. The presence of an allyl group is indicated from the PMR spectrum and from that of the peracetate of 3. Hydrolysis of the glucoside 3 with emulsin gave D-glucose and chavicol. A monoglucopyranoside structure was confirmed by the elemental analysis of 3 tetraacetate and the negative molecular rotation was consistent with

* Part 2 in the series 'Pinus' by DMXD. For Part 1 see Higuchi, R., Aritomi, M. and Donnelly, D. M. X. (1977) *Phytochemistry* **16**, 1007.

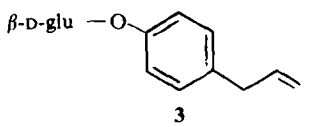
a β-configuration. Compound 11 is therefore chavicol 4-*O*-β-D-glycopyranoside.

A detailed investigation of compound 12 and 13 was not possible due to lack of material. However structures 4 and 5 were assigned respectively on the limited data obtained. From the PMR spectrum of the aglycone of compound 12, obtained by hydrolysis with emulsin, the presence of an allyl group was observed. Elemental analysis of the aglycone showed it to be a monohydroxy-monomethoxyphenylprop-1-ene. The aromatic protons in the PMR spectrum of the Me ether (**4**, R.=.Me) closely resembled those of 2,4-dimethoxybenzyl alochol.





The aglycone therefore had either 2-OH-4-OMe or a 4-OH-2-OMe structure. The mono-*O*-β-D-glucopyranoside character was supported by a negative molecular rotation (−195.6°), elemental analysis and PMR of the peracetate of **4** (R = β-D-glucose). Consequently, compound 12 is either a 2- or a 4-*O*-β-D-glucopyranoside of **4** (R = H).



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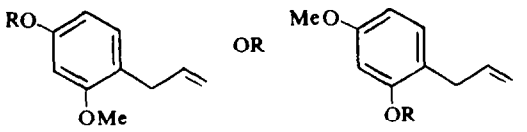
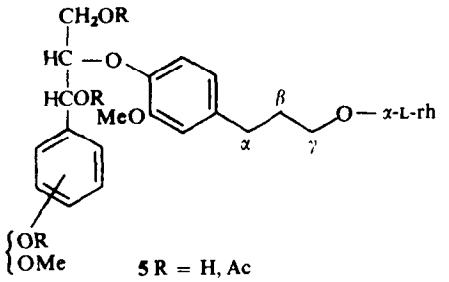


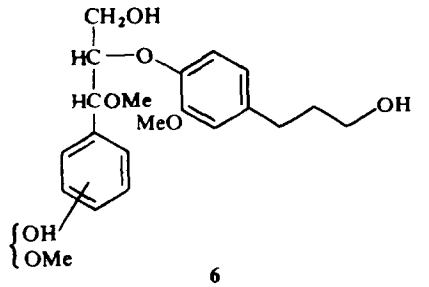
4 R = H, Me, β-D-glu

The acid hydrolysate of compound 13 afforded L-rhamnose dihydroconiferyl alcohol (minor aglycone) and a major fraction, an aglycone (6) which is apparently a mixture of diastereomers. The PMR spectrum of this aglycone shows the presence of one aliphatic and two aromatic OMe groups, 6 aromatic protons and a characteristic doublet at δ 4.50. This one proton doublet and the aliphatic OMe were assigned to C-1. The OMe is thought to result from methylation during the hydrolysis, as this group is not present in the spectra of the glucoside. Methanol was found necessary for solution of the substrate. The peracetate of 13 had a similar PMR to that of a α-L-rhamnopyranoside [7] and a pattern of signals (δ 4.32 (*q*, *J* = 14, 7 Hz) δ 4.49 (*q*, *J* = 14, 5 Hz) δ 4.5 ~ 4.8 (*m*) and δ 618 (*d*, *J* = 5.5 Hz)) resembling those recorded by Ludwig *et al.* [8] for 1-(3,4-dimethoxyphenyl)-2-(2'-methoxyphenoxy)propan-1,3-diol. Based on the above data and on the cooccurrence of related



5 R = H, Ac

phenylpropanol compounds in pine needles, a basic skeleton (6) was considered for the aglycone of compound 13. Compound 13 has the L-rhamnose moiety attached at the γ-carbon as a PMR signal for —CH_2OAc (normally at δ 4.16 (*t*, *J* = 6 Hz)) is absent in the peracetate of 13. Structure (**5**, R = H) is presented as a partial structure for the glycoside 13. A closely related glycoside (**7**) is reported from the leaves of *Thuja plicata* [9].



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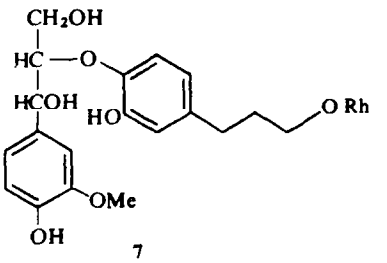
Finally, compound 14 had strong OH and CO absorptions and gave benzoic acid and D-glucose (ratio 1:1) on hydrolysis with emulsin. The pyranoside form of D-glucose and the β-configuration were seen from the PMR spectrum of the glucoside acetate. Compound 14 is 1-*O*-benzoyl-β-D-glucopyranoside. This ester and the preceding mono- and dilignol glycosides with the exception of rheosmin 4-*O*-β-D-glycopyranoside have not been previously recorded.



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EXPERIMENTAL

Details for the general procedures are as described previously [2]. The methods used for acetylation and for hydrolysis with emulsin is described only for compound **8**.

Isolation. The less polar fractions of the extracts (5 g) A, B and C of the water solubles from *Pinus contorta* needles were combined and chromatographed on Si gel (150 g) using ($CHCl_3$–MeOH–H_2O (9:1:0.1)) and separated to give (i) an oil (1 g).

(ii) 3.3 g (iii) 0.7 g. Fraction (i) was not investigated. Fractions (ii) and (iii) were each chromatographed on Sephadex and eluted with H_2O. Fraction (ii) yielded 4 sub-fractions (160 mg; 250 mg; 215 mg; and 360 mg). Each sub-fraction was chromatographed on a Sephadex column, eluted with MeOH and subsequently purified by PLC ($CHCl_3$–MeOH–H_2O (8:2:0.1)) to afford compounds 8 (32 mg), 9 (64 mg), 10 (117 mg), 11 (102 mg), 12 (100 mg) and 13 (60 mg). Fraction (iii) was fractionated to give compound 14 (37 mg), which was further purified by PLC ($CHCl_3$–MeOH–H_2O (8:2:0.1)); and compound 1 (dihydroconiferyl alcohol γ-*O*-β-D-glucopyranoside) [2].

Zingerone 4-O-β-D-*glucopyranoside* (*compound* 8). (1, R = OMe). An oil, $[\alpha]_D^{22°}$ 31.4° (*c* 0.35, MeOH); ν_{max} (neat oil) cm^{-1} 3400, 1710. λ_{max} (MeOH) 275 nm (ε 1241). PMR ($CDCl_3$–CD_3OD): δ 2.2 (3H, s, —C<u>H</u>$_3$), 2.86 (4H, *bs*, —CH_2—CH_2), 3.94 (3H, s, OMe), 6.6–7.3 (3H, *m*, φ-H). Acetylation of 8 (6 mg) with Ac_2O–Py and PLC of the product on Si gel with *n*-hexane–EtOAc (1:1) gave the peracetate (4 mg) as an oil. PMR: δ 1.9–2.1 (12H, sugar OAc × 4), 2.2 (3H, s, C<u>H</u>$_3$), 2.86 (4H, *bs*, —CH_2—CH_2), 3.89 (3H, s, OMe), 4.3 (2H, *m*, glucose 6-H), 5 ~ 5.4 (4H, glucose 1,2,3,4-H), 6.6–7.3 (3H, *m*, φ-H).

Hydrolysis of the glucopyranoside (1, *R = OMe) with emulsin.* Compound 8 (30 mg) in H_2O (5 ml) was incubated with almond emulsin (20 mg) at 37° for 2 hr and the hydrolysate extracted with $CHCl_3$. The $CHCl_3$ layer was washed, dried and evapd. The residue was purified by PLC (*n*-hexane–EtOAc (1:1)) to give zingerone (10 mg) as needles, mp 34–35°. (Found: C, 67.99; H, 7.19. Calc. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%). ν_{max} (Nujol) cm^{-1} 3450, 1710. λ_{max} (MeOH) 381 nm (ε 2561). PMR: δ 2.13 (3H, s, —COC<u>H</u>$_3$), 2.79 (4H, *bs*, —CH_2—CH_2—), 3.88 (3H, s, OMe), 6 (1H, *bs*, OH), 6.6–7.0 (3H, *m*, φ-H) indentical (TLC, PMR, IR) with a synthetic sample of zingerone. The aq. layer was concd and chromatographed on Si gel ($CHCl_3$–MeOH–H_2O (25:17:2)) and Sephadex (MeOH) to give D-glucose (8 mg), $[\alpha]_D^{22°}$ + 49.0 (*c* 0.8, H_2O).

Rheosmin 4-O-β-D-*glucopyranoside* (compound 9) (1, R = H). An oil, $[\alpha]_D^{22°}$ − 48.9° (*c* 0.45, MeOH). ν_{max} (neat) cm^{-1} 3400, 1700. λ_{max} (MeOH) nm (ε) 274 (971) 280 (840). PMR ($CDCl_3$ + CD_3OD): δ2.15 (3H, s, Me), 2.81 (4H, *bs*, —CH_2—CH_2—), 4.9 (1H, *m*, w(h/2) = 10 Hz anomeric-H), 7.1 (4H, *m*, φ-H). 9 (32 mg) gave a peracetate (28 mg) as needles (*n*-hexane), mp 120–123°. PMR: δ 2.0–2.2 (12H, 4-OAc), 2.16 (3H, s, Me), 2.84 (4H, *m*, —CH_2—CH_2—), 3.9 (1H, *m*, glucose 5-H), 4.3 (2H, *m*, glucose 6-H), 5–5.5 (4H, *m*, glucose 1,2,3,4-H), 6.99 (δ_A), 7.24 (δ_B) (4H, *q*, *J* = 9 Hz, A_2B_2 system). Hydrolysis of 9 (32 mg) with emulsin gave D-glucose (9 mg); $[\alpha]_D^{22°}$ + 57.3° (*c* 0.9, H_2O) and rheosmin (6 mg) as needles ($CHCl_3$–*n*-hexane), mp 75–76°. (Found: C, 73.2; H 7.18. Calc. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37%). ν_{max} (Nujol) cm^{-1} 3350, 1700. λ_{max} (MeOH) 279 nm (ε 1681). PMR: δ 2.16 (3H, s, —Me), 2.83 (4H, *bs*, —CH_2—CH_2), 5.6 (1H, *m*, OH), 6.84 (δ_A), 7.17 (δ_B), (4H, *q*, *J* = 9 Hz A_2B_2 system) identical with *p*-hydroxyphenylbutan-2-one (mmp, IR, PMR).

γ-O-*Acetyl-dihydro*-p-*coumaryl alcohol* (compound 10 (2) Needles ($CHCl_3$–Me_2CO), mp 74–76°. (Found: C, 54.84; H, 6.79. $C_{17}H_{24}O_8H_2O$ requires C, 54.54; H, 7.0%). $[\alpha]_D^{23}$ − 41.8 (*c* 1.9, MeOH). ν_{max} (KBr) cm^{-1} 3400, 1710. λ_{max} (MeOH) nm (ε) 273 (2024) 280 (1724). PMR ($CDCl_3$ + CD_3OD): δ 1.9 (2H, *m*, β-CH_2), 2.1 (3H, s, OAc), 2.71 (2H, *t*, *J* = 7 Hz, α-CH_2), 4.14 (2H, *t*, *J* = 6 Hz, γ-CH_2—), 5 (1H, *m*, w(h/2) = 9 Hz anomeric -H, 7.18 (4H, *m*, φ-H). The pentaacetate was an oil. ν_{max} Nujol cm^{-1} 1740–1710. PMR: δ 1.9, 2.2 (15H, 5×OAc), 3.9 (1H, *m*, 5-H glucose), 4.3 (2H, *m*, glucose 6-H), 5–5.5 (4H, *m*, 1,2,3,4-H glucose), 2.7 (2H, *t*, *J* = 7 Hz —CH_2), 4.17 (2H, *t*, *J* = 6 Hz —CH_2—), 7.02 (δ_A), 7.25 (δ_B), (4H, *q*, *J* = 9 Hz A_2B_2 system). 10 (79 mg) was hydrolysed with emulsin (30 mg) to give D-glucose (22 mg) $[\alpha]_D^{25°}$ + 51.8° (*c* 1.1, H_2O) and γ-acetoxydihydro-*p*-coumaryl alcohol (25 mg) as an oil. ν_{max} (Nujol) cm^{-1} 3400, 1710. PMR: δ 2 (2H, *m*, β-CH_2—), 2.67 (2H, *t*, *J* = 7 Hz, α-CH_2—), 4.16 (2H, *t*, *J* = 6 Hz, γ-CH_2—), 6.04 (1H, *bs*, φ-OH), 6.87 (δ_A), 71.6 (δ_B), (4H, *q*, *J* = 9 Hz A_2B_2 system).

Hydrolysis of 10 with alkali. Compound 10 (35 mg) was refluxed with Na_2CO_3 in MeOH (95%) for 20 min, filtered and the reaction mixture was evapd. The residue was purified by PLC ($CHCl_3$–MeOH–H_2O (8:2:1)) to yield dihydro-*p*-coumaryl alcohol 4-*O*-β-D-glycopyranoside as needles from Me_2CO, mp 130–132° (identical mp, TLC with authentic sample).

Chavicol 4-O-β-D-*glucopyranoside* (compound 11) (3). An amorphous solid, $[\alpha]_D^{20°}$ − 53.1° (*c* 0.65, MeOH). λ_{max} (MeOH) nm (ε) 253 (2778) 271 (1366) 280 (1002). PMR ($CDCl_3$ + CD_3OD): δ5.1 (2H, *bd*, *J* = 13 Hz, =CH_2), 6 (1H, *bm*, —CH=), 7.14 (4H, *m*, φ-H). The peracetate was purified by PLC (*n*-hexane–EtOAc (3:2)) and gave needles from MeOH, mp 136–138°. (Found: C, 59.30; H, 5.86. $C_{23}H_{28}O_{10}$ requires C, 59.47; H, 6.08%) ν_{max} (Nujol) 1750 cm^{-1}. PMR: δ 2–2.2 (12H, 4 × *s* OAc), 3.41 (2H, *d*, *J* = 6.5 Hz φ-CH_2—), 3.9 (1H, *m*, glucose 5-H), 4.3 (2H, *m*, glucose 6-H), 4.9–5.5 (6H, *m*, glucose 1,2,3,4-H and =CH_2), 6 (1H, *m*, —CH=), 7.03 (δ_A), 7.26 (δ_B), (4H, *q*, *J* = 9 Hz A_2B_2 system). Hydrolysis of 11 (48 mg) with emulsin (20 mg) gave D-glucose (18 mg) $[\alpha]_D^{20°}$ + 46.11° (*c* 0.36, H_2O) and chavicol (10 mg) chavicol was purified by PLC (*n*-hexane–EtOAc (3:1) and gave an oil λ_{max} (MeOH) 279 nm (ε 1581). PMR: δ 3.39 (2H, *d*, J = 6 Hz, φ-CH_2—), 5.12 (2H, *bd*, *J* = 13 Hz, =CH_2), 4.93 (1H, *m*, OH), 6 (1H, *bm*, —CH=), 6.86 (δ_A), 7.18 (δ_B), (4H, *q*, *J* = 9 Hz A_2B_2 system).

2(or *4*)-*Methoxyphenylprop-1-ene 4 (or 2)* O-β-D-*glucopyranoside* (compound 12). Needles (H_2O), mp 79–81° $[\alpha]_D^{16°}$ − 60.0 (*c* 0.3, H_2O) λ_{max} (MeOH) nm (ε) 277 (2119) 283 (1847). PMR ($CDCl_3$ + CD_3OD): δ 3.82 (3H, s, OMe), 5.07 (2H, *bd*, *J* = 13 Hz, =CH_2), 6 (1H, *bm*, —CH=), 6.62 (1H, *q*, *J* = 2,9 Hz, φ-H). 6.83 (1H, *J* = 2 Hz, φ-H), 7.14 (1H, *d*, *J* = 9 Hz, φ-H). The peracetate was obtained as needles (*n*-hexane–$CHCl_3$), mp 118–119° (Found: C, 58.57; H, 6.38. $C_{24}H_{30}O_{11}$ requires C, 58.29; H, 6.12%) ν_{max} (Nujol) 1750 cm^{-1}. PMR: δ 2–2.2 (12H, 4 × *s*, OAc), 3.29 (2H, *d*, *J* = 6 Hz, φ—CH_2—), 3.82 (3H, s, OMe), 3.9 (1H, *m*, glucose 5-H) , 4.3 (2H, *m*, glucose 6-H), 4.8–5.6 (6H, *m*, glucose 1,2,3,4-H and =CH_2), 6 (1H, *bm*, —CH=), 6.66 (1H, *q*, *J* = 2, 8 Hz, φ-H), 6.75 (1H, *d*, *J* = 2 Hz, φ-H), 7.16 (1H, *d*, *J* = 8 Hz, φ-H), Hydrolysis of 12 with emulsin gave D-glucose $[\alpha]_D^{15°}$ + 42.5° (*c* 0.36, H_2O) and an aglycone as an oil. λ_{max} (MeOH) 280 nm (ε 2314). PMR: δ 3.37 (2H, *d*, *J* = 6 Hz, φ-CH_2—) 3.78 (3H, s, OMe), 4.9–5.5 (3H, *m*, =CH_2 and OH), 6 (1H, *bm*, —CH=), 6.48 (1H, *d*, *J* = 2 Hz, φ-H), 6.52 (1H, *q*, *J* = 2, 9 Hz, φ-H), 7.07 (1H, *d*, *J* = 9 Hz, φ-H). The Me ether of the aglycone (16 mg) was obtained by methylation with NaH, MeI and DMSO (Hakomori) and purified by PLC (*n*-hexane–EtOAc (4:1)) to afford an oil (13 mg). PMR: δ 3.37 (2H, *d*, *J* = 6.5 Hz, φ-CH_2—), 3.86 (6H, *s*, 2 × OMe), 5.08 (2H, *bd*, *J* = 13 Hz, =CH_2), 6 (1H, *bm*, —CH=), 6.49 (1H, *q*, *J* = 2, 9 Hz, φ-H) 6.52 (1H, *d*, *J* = 2 Hz, φ-H), 7.12 (1H, *d*, *J* = 9 Hz, φ-H).

Compound 13 (5, R = H). Amorphous powder, chromatographically homogenous, $[\alpha]_D^{19°}$ − 26.0 (*c* 0.25, MeOH). λ_{max} (MeOH) 280 nm (ε 5450). PMR ($CDCl_3$ + CD_3OD): δ 1.29 (3H, *d*, *J* = 6 Hz, rhamnose 5-Me), 1.9 (2H, *m*, β-CH_2—), 2.69 (2H, *t*, *J* = 7 Hz, α-CH_2—), 3.96 (6H, s, OMe), 4.77 (1H, s, rhamnose 1-H), 4.99 (1H, *d*, *J* = 6 Hz, φ-C<u>H</u>(OH)—COH—), 6.6–7.3 (6H, *m*, φH). The peracetate was an oil $[\alpha]_D^{21}$ − 26.5° (*c* 0.2, $CHCl_3$), λ_{max} ($CHCl_3$) 278 nm (ε 5044). PMR: δ 1.22 (3H, *d*, *J* = 6 Hz rhamnose 5-Me), 1.9–2.2 (15H, 5 × OAc), 2.33 (3H, s, φ-OAc), 2.7 (2H, *t*, *J* = 7 Hz, α-CH_2—), 3.83, 3.87 (6H, s, 2 × OMe), 4.32 (1H, *q*, *J* = 14, 4 Hz, —CH—C<u>H</u>$_2$—OAc), 4.49 (1H, *q*, *J* = 14, 5 Hz —CH—CH_2OAc), 4.5–4.8 (1H, *m*, 2-CH), 5.13 (1H, *t*, *J* = 9 Hz rhamnose 4-H), 5.33 (1H, s, rhamnose 2-H), 5.43 (1H, *q*, *J* = 9, 3 Hz rhamnose 3-H), 6.18 (1H, *d*, *J* = 5.5 Hz, 1-C<u>H</u>(OAc), 6.5–7.3 (6H, *m*, φ-H), 4.79 (1H, s, rhamnose 1-H).

Acid hydrolysis of 13. Compound 13 (50 mg) was refluxed with 2N HCl in MeOH (50%) for 30 min, the reaction mixture diluted with H_2O and extracted with EtOAc. The EtOAc layer was washed, dried and evapd. The residue was fractionated on PLC (EtOAc) to give oils. The minor fraction (trace) was identified as dihydroconiferyl alcohol. The major fraction (6) (10 mg), PMR: δ 1.99 (2H, *m*, β-CH_2—), 2.7 (2H, *m*, φ-CH_2—), 3.37 (3H, s, OMe), 3.9–4.1 (6H, *m*, 2 × OMe), 4.5 (1H, *d*, *J* = 7 Hz, φ-CH(OMe), 6.5–7.5 (6H, *m*, φ-H). The triacetate (9 mg)

was an oil, λ_{max} ($CHCl_3$) nm (ε) 2.80 (4308) 278 (4250). PMR: δ 1.8 (2H, *m*, β-CH_2—), 2–2.2 (6H, *m*, 2 × OAc), 2.35 (3H, *s*, ϕ-OAc), 2.68 (2H, *t*, J = 7 Hz —CH_2—), 3.4 (3H, *s*, OMe), 3.75–3.95 (6H, *m*, 2 × OMe), 4.16 (2H, *t*, J = 6 Hz, γ-CH_2), 4.51 (2H, *bs*, —COH—CH_2OAc), 6.6–7.3 (6H, *m*, ϕ-H).

The aq. layer from the hydrolysis was neutralised with Amberlite IR-45, evapd *in vacuo* and the residue hydrolysed with N HCl for 1.5 hr. The hydrolysate was neutralised, concd and the residue chromatographed on Si gel ($CHCl_3$–MeOH–H_2O (25:17:2)) and Sephadex LH 20 (MeOH) to give L-rhamnose, $[\alpha]_D^{22°}$ + 6.0° (*c* 0.2, H_2O).

1-O-Benzoyl-β-D-glucopyranoside (compound 14). Prisms, mp 191–192° (Found: C, 54.37; H, 5.48. $C_{13}H_{16}O_7$ requires C, 54.93; H, 5.67%) ν_{max} (KBr) cm^{-1} 3400, 1730. PMR ($CDCl_3$ + CD_3OD) δ5.65 (1H, *m*, w(h/2) = 10 Hz anomeric-H, glucose), 7.15–7.6 (3H, *m*, ϕ-H), 8.1 (2H, *m*, ϕ-H). The tetraacetate crystallised as needles (MeOH), mp 140–142°. PMR: δ 1.9–2.2 (12H, 4 × OAc), 4.06 (1H, *m*, glucose 5-H), 4.3 (2H, *m*, glucose 6-H), 5–5.6 (3H, *m*, glucose 2,3,4-H), 6.05 (1H, *m*, w(h/2) = 9 Hz, anomeric-H), 7.3–7.7 (3H, *m*, ϕ-H), 8.06 (2H, *m*, ϕ-H). Hydrolysis of 14 with emulsin yielded benzoic acid and glucose which were identified by TLC.

Synthesis of authentic samples. Zingerone. A soln of vanillin (6.7 g) in Me_2CO (30 ml) was treated with 10% NaOH (30 ml) and kept at 18° for 4 days. The reaction mixture was acidified and then evaped to give a yellow ppt. which was collected, washed with H_2O and crystallised from aq. EtOH to give 3-hydroxy-4-methoxyphenylprop-3-en-2-one (3.5 g) as prisms, mp 124–127°. (Found: C, 68.82; H, 6.40. Calc. for $C_{11}H_{12}O_3$, C, 68.73; H, 6.29%) ν_{max} (Nujol) cm^{-1} 3300, 1675. λ_{max} (MeOH) nm (ε) 336 (15,943) 240 (7,886). PMR: δ 2.39 (3H, *s*, Me) 3.95 (3H, *s*, OMe), 6.67 (1H, *d*, J = 16 Hz, 3-H), 7.59 (1H, *d*, J = 16 Hz, 4-H), 6.9–7.3 (3H, *m*, ϕ-H). This product (500 mg) was hydrogenated with Pd/C (170 mg) in $CHCl_3$ and the reaction mixture purified by PLC (*n*-hexane–EtOAc (3:1)) to give 3 compounds. The major product zingerone had indentical PMR, IR and TLC with the aglycone of compound 8. Two minor products were 2-methoxy-4-(3-hydroxybutyl)phenol (187 mg) and 2-methoxy-4-butylphenol (50 mg). *Rheosmin.* Base catalysed condensation of *p*-hydroxybenzaldehyde (7 g) and Me_2CO (30 ml) yielded *p*-hydroxyphenylprop-3-en-2-one (3.11 g) as yellow plates (*n*-hexane–EtOAc), mp 95–97°. (Found: C, 74.37; H, 6.32. Calc. for $C_{10}H_{10}O_2$, C, 74.05; H, 6.22%). ν_{max} (Nujol) cm^{-1} 3140, 1660, λ_{max} (MeOH) nm (ε) 321 (17994) 233 (7811). PMR: δ 2.44 (3H, *s*, Me), 6.69 (1H, *d*, J = 17 Hz; 3-H), 7.67 (1H, *d*, J = 17 Hz, 4-H), 7.04, (δ_A) 7.55, (δ_B), (4H, *q*, J = 9 Hz, A_2B_2 system). Hydrogenation with Pd/C (10%) gave 3 products. The major product (314 mg) needles (*n*-hexane–$CHCl_3$), mp 78–79° was identical with the aglycone from compound **9**; the minor products were *p*-hydroxyphenylbutane (63 mg) and *p*-hydroxyphenylbutan-2-ol (150 mg).

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