Further Phenolic Components from *Alnus japonica* Steud.

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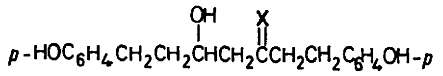
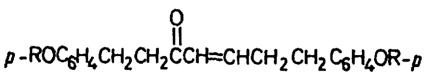
Summary Further investigation of the phenolic components of the wood of *Alnus japonica* Steud. show that bridged biarylheptanoids are accompanied by their open-chain counterparts, the supposed biogenetic precursors.

Further extraction on a larger scale of the phenolic components of the wood of *Alnus japonica* Steud.[1] has led to the isolation of three open-chain and one bridged biarylheptanoids in addition to the three biarylheptanoids *reported previously*.



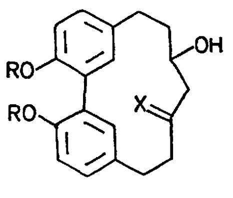
$p\text{-HOC}_6\text{H}_4\text{CH}_2\text{CH}_2\overset{\text{OH}}{\overset{|}{\text{C}}}\text{HCH}_2\overset{\text{X}}{\overset{\|}{\text{C}}}\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OH-}p$

(I) X = O
(II) X = H, OH

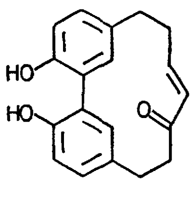


$p\text{-ROC}_6\text{H}_4\text{CH}_2\text{CH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH=CHCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OR-}p$

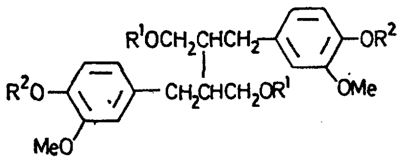
(III) R = H
(IV) R = Me

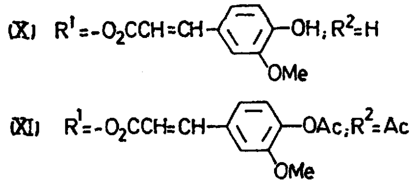


(V) X = β-H, α-OH; R = H
(VI) X = β-H, α-OH; R = Ac
(VII) X = O; R = H
(VIII) X = α-H, β-OH; R = H



(IX)





(XII) R^1 = R^2 = H

Two of the three open-chain compounds are known, namely compounds (I),[2,3] m.p. 139—140°, and (II),[3] m.p. 165—166°, and these were characterized by spectral comparison. Compound (I) was isolated previously from the green bark of *Betula platyphylla Sukatch. var japonica* Hara as a glucoside[2] and also from the wood of *A. hirsuta* Turcz. in the free state.[3] Compound (II) was also found in the latter. The new unbridged biarylheptanoid compound (III) was obtained as an oil, ν_{max} 1685 and 1658 cm^{-1}, δ ($CDCl_3$–CD_3OD) 2·48 (2H, t, *J* 7 Hz), 2·66 (2H, t, *J* 7 Hz), 2·77 (4H, s), 6·03 (1H, br d, *J* 16 Hz), 6·80 (1H, br d, *J* 16 Hz), and 6·72 and 6·96 (8H, AB q, J_{AB} 8 Hz). These data indicate structure (III) and this has been confirmed by synthesis of its methyl ether (IV), m.p. 50—51°, from

3-(*p*-methoxyphenyl)propionylmethylene phosphorane and 3-(*p*-methoxyphenyl)propionaldehyde.

The new bridged biarylheptanoid alnusdiol (V) had m.p. $>300°$, $[\alpha]_D$ $-46{\cdot}7°$ (*c* 0·52, EtOH), $C_{19}H_{22}O_4$ (M^+ 314), ν_{max} 3450 and 3280 cm^{-1}, δ (C_5D_5N) 1·80—2·20 (2H, m), 2·20—2·73 (4H, m), 2·73—3·6 (4H, m), and 4·47 (2H, m), and yields a tetra-acetate, m.p. 159—162°, spectral data for which suggest that it may be a diol corresponding to alnusonol (VII).[1] Treatment of (VII) with $LiAlH_4$ in tetrahydrofuran afforded (V) and compound (VI), m.p. 244—247°, $[\alpha]_D$ 0° (*c* 0·25, EtOH) in *ca.* 2: 1 ratio. Reduction of (VII) with $NaBH_4$ in alkaline methanol afforded (VI) almost solely. A molecular model shows that the carbonyl group in (VII) is almost perpendicular to the plane of the molecule and the bulkier species in the latter reduction would be more prone to attack this group from the less hindered *exo* direction.[4]

Our present and previous results[1] together indicate that the bridged biarylheptanoids, alnusone (IX), alnusonol (VII), and alnusdiol (V) co-exist in the same plant with the corresponding open-chain compounds, (III), (I) and (II). This constitutes the first clear-cut demonstration of the biogenetic relationship between both types of compound, which has been suggested by many workers.[1,4,5]

Other phenylpropanoid compounds, vanilic acid and secoisolariciresinol diferulate (X) are also obtained. Compound (X) had m.p. 204—205°, $[\alpha]_D$ $-52{\cdot}5°$ (*c* 0·65, pyridine), $C_{40}H_{42}O_{12}$, ν_{max} 3400 and 1700 cm^{-1} and yielded an oily tetra-acetate (XI), which gave spectral data consistent with this formulation. Alkaline hydrolysis of (X) afforded ferulic acid and a lignan diol (XII), m.p. 119—120°, $[\alpha]_D$ $-19{\cdot}7°$ (*c* 0·89, pyridine).[6]

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