

Three New Cyclized C₉-C₁-C₉ Compounds from *Alnus japonica* Steud.

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Summary The wood of *Alnus japonica* Steud. has been found to contain three cyclized C₉-C₁-C₉ phenols; alnusone (I), alnusonol (II), and alnusoxide (III).

ON chromatography (SiO₂) the phenolic extractive of the wood of *Alnus japonica* Steud. gave three crystalline compounds which are designated as alnusone (I), alnusonol (II), and alnusoxide (III) respectively. We report here on their structures.

Alnusone (I), C₁₉H₁₈O₃ (*M*⁺ 294), m.p. 253—255° has two phenolic hydroxy-groups and a conjugated ketone system [ν_{\max} (Nujol) 3300, 1680, 1608, and 1505 cm⁻¹; λ_{\max} (EtOH) 217 (ϵ 22,000), 239 (sh., 16,700), and 300 nm (7200); λ_{\max} (NaOH-EtOH) 218 (ϵ 24,000), 254 (sh., 19,800), and 327 nm

(14,400)], and forms a diacetate (IV), m.p. 233—236°; [ν_{\max} (Nujol) 1755, 1692, and 1610 cm⁻¹; δ (CDCl₃) 2.16 (6H, s)]. The presence of an ethylenic double bond conjugated to the ketone group was demonstrated by the production of dihydro-compounds (V), [λ_{\max} (EtOH) 249 (sh., ϵ 8580) and 303 nm (5680); ν_{\max} (Nujol) 1700 cm⁻¹], and (VI), [ν_{\max} (Nujol) 1755 and 1702 cm⁻¹] on hydrogenation (Pd-C) of (I) and (IV) respectively. The appearance of a doublet (*J* 15.5 Hz) at δ 6.30 in the n.m.r. spectrum of (I) suggests that the double bond is *trans* disubstituted. Integration of the aromatic n.m.r. signals (δ 6.64—7.12) shows seven protons, including the β -hydrogen of the conjugated ketone system. In the n.m.r. spectrum of (IV), with added Eu(dpm)₃, two sets of AMX signals with the same coupling

constants ($J_{AM} = ca. 0$, $J_{AX} = 3$ and $J_{MX} = 9$ Hz) were observed, which indicates the presence of two 1,3,4-trisubstituted benzene rings in (I). The u.v. spectrum of dihydroalnusone (V) is very similar to that of 2,2'-dihydroxybiphenyl¹ and hence alnusone (I) is deduced to contain this chromophore. The n.m.r. spectrum of (I) also shows 2 OH (δ 7.49) and 4 CH₂ signals (δ 2.96—3.28). With this information, structures (I) or (Ia) would be plausible for alnusone. However (Ia) is not consistent with the n.m.r. spectrum of alnusone which exhibits all four CH₂ signals at very similar fields, lower than δ 2.96.† Structure (I) for alnusone has been confirmed by chemical reactions. Ozonolysis of alnusone diacetate (IV) followed by hydrolysis and methylation (MeI—K₂CO₃—acetone) afforded dimethyl 6,6'-dimethoxybiphenyl-3,3'-dipropionate² which was identified by comparison with an authentic sample (i.r. and t.l.c.). Thus alnusone is assigned conclusively structure (I). Compounds of this type have previously been described; asadanin (VII) from *Ostrya japonica* Sarg. (Betulaceae)³ and myricanone (VIII) and myricanol (IX) from *Mirica nagi* (Myricaceae)⁴.

Alnusonol (II), m.p. 171—173° has a molecular formula C₁₉H₂₀O₄ (M^+ 312), which suggests (II) might be a hydrated form of (I). Thus (II) shows i.r. peaks at 3410, 3120, (OH) and 1700 (saturated ketone) cm⁻¹ and exhibits a multiplet from CHOH at δ 4.30. The u.v. spectrum of (II) closely resembles that of (V). Upon acetylation with acetic anhydride and pyridine at room temperature (II) yielded alnusone diacetate (IV). The readiness of the elimination suggests that the hydroxy-group in (II) is β to the ketonic group. Therefore alnusonol is reasonably assigned structure (II).

Alnusoxide (III), C₁₉H₁₈O₄ (M^+ 310), m.p. 266—269° contains one more oxygen atom than alnusone (I). The u.v. spectrum indicates the presence of the same chromophore in (III) as in (II) and (V). Compound (III) displays CO i.r. absorption at 1710 cm⁻¹. Since it was presumed that (III) could be the epoxide of (I), the latter was oxidized with alkaline hydrogen peroxide at room temperature. The product is, in fact, identical with (III), providing conclusive evidence for the structure of this compound.

The structures of (I), (II), and (III) are biogenetically interesting in view of the reported occurrence of acyclic C₉—C₁—C₉ compounds† in *Alnus firma* Sieb. et Zucc.^{5,6} Clearly

† Cf. the n.m.r. data of yashabushi-ketol in ref. 6.

‡ A pertinent survey of C₉—C₁—C₉ compounds and their biogenesis is described in J. M. Edwards, R. C. Schmitt, and U. Weiss, *Phytochemistry*, 1972, **11**, 1717.

¹ K. Bowden and C. H. Reece, *J. Chem. Soc.*, 1950, 2249.

² E. Fujita, K. Fuji, and K. Tanaka, *J. Chem. Soc.*, (C), 1971, 205.

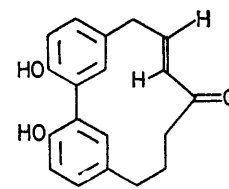
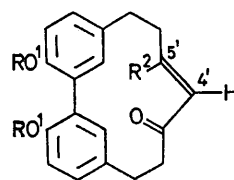
³ M. Yasue, *Mokuzai-gaku-Kaishi*, 1965, **11**, 146, 152. The conclusion of the second reference stated here is misquoted in *Chem. Abs.*, 1966, **65**, 2163. The acyclic structure should be (VII) as in the original reference.

⁴ R. V. M. Campbell, L. Crombie, B. Tuck, and D. A. Whiting, *Chem. Comm.*, 1970, 1206; M. J. Begley and D. A. Whiting, *ibid.*, 1970, 1207.

⁵ Y. Asakawa, F. Genjida, S. Hayashi, and T. Matsuura, *Tetrahedron Letters*, 1969, 3235.

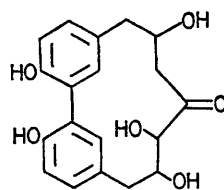
⁶ Y. Asakawa, *Bull. Chem. Soc. Japan*, 1970, **43**, 2223.

(I), (II), (III), and also (VII), (VIII), and (IX) would be formed from an acyclic precursor *via* oxidative coupling catalysed by peroxidase.

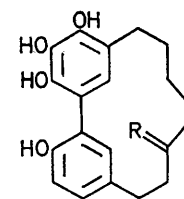


(Ia)

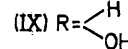
- (I) R¹ = R² = H
 (II) R¹ = H, R² = OH, Δ^{4,5'} saturated
 (III) R¹ = R² = H, 4',5'-epoxy-compound
 (IV) R¹ = Ac, R² = H
 (V) R¹ = R² = H, Δ^{4,5'} saturated
 (VI) R¹ = Ac, R² = H, Δ^{4,5'} saturated



(VII)



(VIII)



(IX)

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Added in proof: After submission of the manuscript, Professor Yasue informed us that he has also characterised six compounds related to asadanin from *Ostrya japonica* Sarg., [M. Yasue, *Bulletin of the Government Forest Experiment Station*, No. 209 (1968)].

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