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BIARYLHEPTANOIDS AND OTHER CONSTITUENTS FROM WOOD OF *ALNUS JAPONICA*

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Key Word Index—*Alnus japonica*; Betulaceae; new biarylheptanoids; biosynthesis; chemotaxonomy; secoisolariciresinol diferulate; steroids; oleanan triterpenoids.

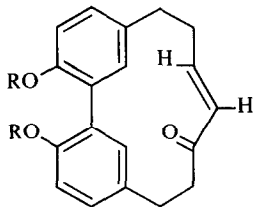
Abstract—The wood of *Alnus japonica* has been shown to contain a number of biarylheptanoids as well as other phenolics, including secoisolariciresinol diferulate. The co-occurrence of cyclized biarylheptanoids with their corresponding acyclic biarylheptanoids has been demonstrated and this fact may have biosynthetic significance. The possible chemotaxonomic importance of biarylheptanoids in members of the Betulaceae is discussed. The isolation and identification of several steroids and triterpenoids are also described.

INTRODUCTION

Alnus japonica Steud. is a deciduous tree which is found in the damp parts of the fields and forests of Japan. We are interested in the deep yellow colour of this tree, and in an attempt to clarify the precursor of the colouring matter we have investigated the phenolic constituents of the wood [1, 2]. As a result, a number of biarylheptanoids have been isolated, as well as other phenolics. The examination of the neutral components was also carried out.

RESULTS AND DISCUSSION

The shavings of the dry wood of *A. japonica* were extracted with hot MeOH and the extract taken up in EtOAc. The phenolic portion was extracted with 5%



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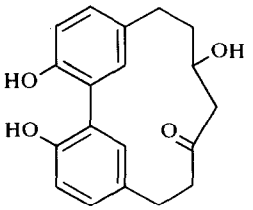
17 R = Me



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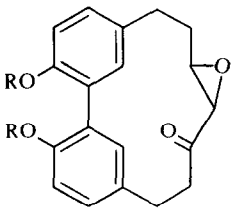

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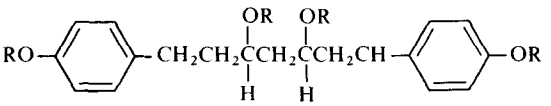

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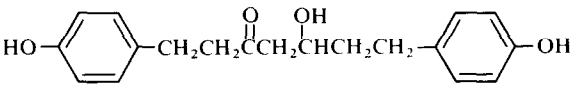

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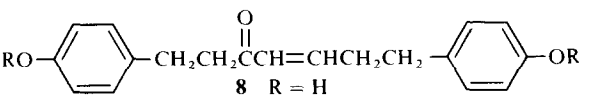

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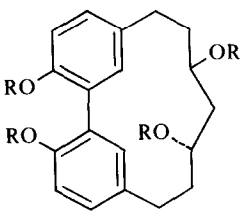

5 R = H
18 R = Ac

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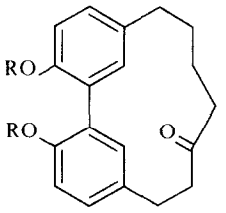
aqueous NaOH and then separated by Si gel chromatography to give five biarylheptanoids: alnusone (**1**), alnusonol (**2**), alnusoxide (**3**), alnusdiol (**5**) and 1,7-bis[4-hydroxyphenyl]heptan-3,5-diol (**6**). On another occasion, the green wood was extracted with cold MeOH which was washed with *n*-hexane prior to extraction with EtOAc. Si gel chromatography of this extract afforded two additional acyclic biarylheptanoids, 1,7-bis[4-hydroxyphenyl]-3-hepten-5-one (**7**) and 1,7-bis[4-hydroxyphenyl]heptan-3-on-5-ol (**8**) as well as other phenolic substances including secoisolariciresinol diferulate (**27**). Si gel chromatography of the *n*-hexane fraction gave several steroids and triterpenoids in addition to further amounts of the biarylheptanoids **1** and **6**, and the lignan ester **27**.

Biarylheptanoids

Alnusone (**1**), $C_{19}H_{18}O_3$ ($M^{+\cdot}$ 294), mp 253–255°, gave a green colour with $FeCl_3$ and was positive to Brady's reagent. The IR spectrum exhibited absorption bands at 3300 (OH), 1680, 1608 (conjugated ketone) and 1608 and 1505 cm^{-1} (aromatic ring). The presence of a phenolic ring was supported by the absorption maxima in the UV spectrum at 217, 239 (sh) and 300 nm, which shifted upon the addition of alkali to 218, 254 (sh) and 327 nm. Since **1** yielded the diacetate **9** on treatment with acetic anhydride and pyridine, and the NMR spectrum of **9** exhibited a signal (δ 2.16) corresponding to two acetate methyls, **1** was presumed to contain two phenolic hydroxyl groups. On catalytic reduction, **1** and **9** afforded the corresponding dihydro derivatives **10** (ν_{max} 1700 cm^{-1}) and **11** (ν_{max} 1702 cm^{-1}), respectively. The appearance of a doublet (J = 15.5 Hz) at δ 6.30 in the NMR spectrum of **1** suggested that the double bond conjugated to the ketone group was *trans*-disubstituted. Integration of the aromatic NMR signals (δ 6.64–7.12) revealed seven protons including the β-proton of the conjugated ketone system. In the NMR spectrum of **9**, with added $Eu(dpm)_3$, two sets of AMX signals with the same coupling constant ($J_{AM} = ca\,0$, $J_{AX} = 3$ and $J_{MX} = 9$ Hz) were observed, indicating the presence of two 1,3,4-trisubstituted phenyl rings in **1**. The UV spectrum of dihydroalnusone (**10**) resembled that of 2,2′-dihydroxybiphenyl [3] and thus the two phenyl rings in **1** must be based on the latter structure. This deduction was supported by the presence of the base peak at *m/z* 211 in the MS of **1**, which corresponded to the fragmentation ion **12**. The generation of **12** was also observed in the mass spectra of the acetates **9** and **11** (relative intensity 100 and 73, respectively). The NMR spectrum of **1** also showed signals due to four methylene groups (δ 2.32–3.24). From the evidence outlined above, alnusone could have structure **1** or **13**. The former structure was assigned to alnusone because all four methylene signals in the NMR spectrum appeared at rather narrow field below δ 2.40, whereas in the case of **13** a methylene signal should be observed near δ 1.8 (cf. **10**



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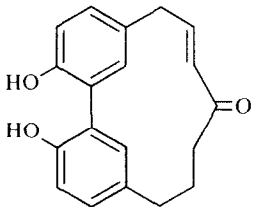

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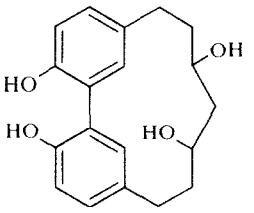

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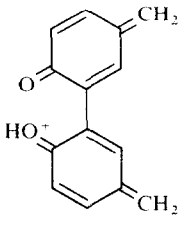

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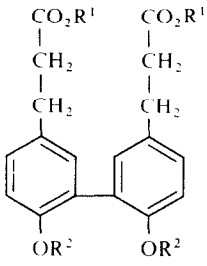
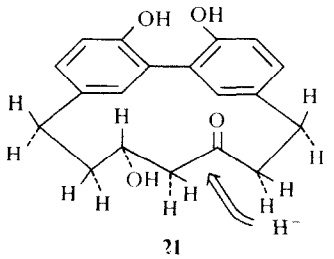


14 R^1 = H, R^2 = Ac
15 R^1 = R^2 = H
16 R^1 = R^2 = Me



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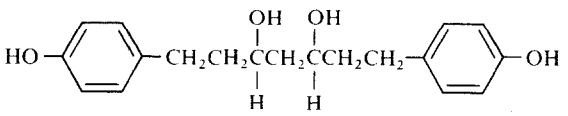


23

which exhibited a four-proton multiplet at δ 1.88). The position of the conjugated ketone system in the aliphatic chain in alnusone (**1**) was confirmed by chemical degradation. Alnusone diacetate (**9**) was ozonized in HOAc and the resultant dicarboxylic acid, **14**, obtained after alkaline hydrolysis was methylated with methyl iodide and K_2CO_3 in acetone. The product was identified as dimethyl 6,6'-dimethoxybiphenyl-3,3'-dipropionate (**16**) by comparison with an authentic sample [4]. Thus the biarylheptanoid structure **1** for alnusone was established. A total synthesis of alnusone dimethyl ether (**17**) has been published [5].

Alnusonol (**2**), $C_{19}H_{20}O_4$ ($M^{+\cdot}$ 312), mp 171–173°, had IR absorption bands at 3410, 3120 (OH) and 1700 cm^{-1} (saturated ketone) and was presumed to be a hydrated form of alnusone (**1**). Its MS exhibited an $[M-18]^+$ peak (33%) as well as one corresponding to the ion **12** (100%). The NMR signal due to the proton attached to the carbon bearing the hydroxyl group was observed at δ 4.30. Upon acetylation with acetic anhydride and pyridine at room temperature, **2** gave alnusone diacetate (**9**). The ease of dehydration was in keeping with the assumption that **2** had a β-hydroxyketone structure corresponding to the α,β-unsaturated ketone system. Therefore structure **2** was assigned to alnusonol.

Alnusoxide (**3**), $C_{19}H_{18}O_4$ ($M^{+\cdot}$ 310), mp 266–269°, contained one more oxygen atom than alnusone (**1**) and was converted to the diacetate **4** upon acetylation. The IR spectra of **3** and **4** contained carbonyl absorption bands at 1710 and 1729 cm^{-1} respectively, and it was presumed that **3** might be the epoxide of alnusone (**1**). Treatment of **1** with alkaline H_2O_2 at room temperature yielded **3**, thus verifying that alnusoxide has structure **3**.

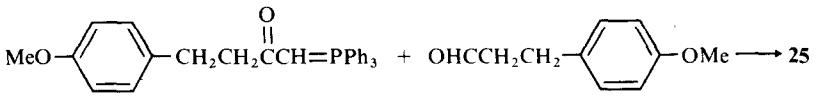
Alnusdiol (**5**), $C_{19}H_{22}O_4$ ($M^{+\cdot}$ 314) had mp > 300° and $[\alpha]_D$ −46.7° (*c*, 0.52, EtOH). Its IR and NMR spectra showed hydroxyl absorptions at 3450 and 3280 cm^{-1} and a multiplet due to two methine protons next to the hydroxyl groups at δ 4.47. The MS of **5** contained an intense peak at *m/z* 294, corresponding to loss of water from the parent ion. On acetylation, **5** furnished a tetraacetate **18**, mp 159–162°, the NMR spectrum of which exhibited two six-proton signals at δ 1.99 and 2.23 and a two-proton multiplet at δ 4.87. These corresponded to the presence of two secondary acetoxyl and two phenolic acetoxyl groups. The afore-mentioned data suggested that **5** might be one of the diastereomeric diols which can be formed from alnusonol (**2**). The presence of optical activity in alnusdiol was in conformity with the *trans*-diol structure **5**. Reduction of **2** with $LiAlH_4$ afforded **5** and the *meso*-diol **19**, mp 244–247°, $[\alpha]_D$ 0° (*c* 0.25, EtOH) in about a 2:1 ratio. Treatment of **2** with $NaBH_4$ produced mainly **19**. Inspection of a molecular model showed that the most probable conformation of the carbonyl group was nearly perpendicular to the plane of the molecule, the hydroxyl group projecting in an *exo* direction (cf. **21**). The large steric requirement in the $NaBH_4$ reduction [6] would favour the reaction proceeding from the less hindered *exo* direction [7].

Compounds **6**, mp 165–166° and **7**, mp 139–140° were identified as hannokinol [8] and hannokinin [8, 9] respectively from their spectral data (see Experimental). Hannokinol (**6**) had been isolated previously from the wood of *Alnus hirsuta* Turcz [8]. Hannokinin (**7**) had been obtained from the same source [8] and was also isolated as a glucoside from green bark of *Betula platyphylla* Sukatch. var. *japonica* Hara [9]. $NaBH_4$ reduction of hannokinin (**7**) furnished hannokinol (**6**) and the corresponding *meso*-diol **23** in approximately equal amounts.

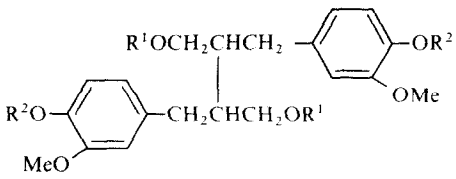
Compound **8**, obtained as an oil, exhibited IR absorption peaks at 3360, 1685 and 1658 cm^{-1}, indicating the presence of the hydroxyl group and a conjugated ketone system. The NMR spectrum revealed the presence of two $-CH_2CH_2-$ groupings (2 H triplets at δ 2.48 and 2.66, J = 7 Hz, and a 4 H singlet at δ 2.77), a *trans*-disubstituted double bond (two broad doublets at δ 6.03 and 6.80, J = 16 Hz) and two *para*-substituted aromatic rings (an 8 H AB quartet at δ 6.72 and 6.96, J = 8 Hz). **8** gave an oily diacetate (**22**) on acetylation with acetic anhydride and pyridine, and a crystalline dimethyl ether (**25**), mp 50–51°, on methylation with methyl iodide, K_2CO_3 and acetone. Confirmation of the structure of **8** was provided by the synthesis of its dimethyl ether (**25**) from 3-[4-methoxyphenyl]propionylmethylenephosphorane (**27**) and 3-[4-methoxyphenyl]propionaldehyde (**26**) (Scheme 1).

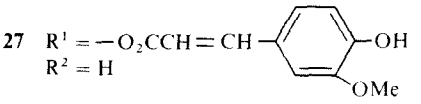
The biarylheptanoids obtained from the dry and the green wood showed some difference in types and relative amounts. The isolation of alnusoxide (**3**) only from dry wood indicated that it was formed during air-drying. The ratio between the amounts of alnusone (**1**) and alnusonol (**2**) was reversed in the dry and the green wood (cf. Experimental). This fact suggested that alnusone was an artefact produced from alnusonol (**2**) on storage and extraction. The same argument can be applied to the relationship of the acyclic compound **8** to **7**. Since alnusone **1** and **8** were obtained in considerable amounts, even in the extraction of the green wood under mild conditions involving only solvent percolation, we believe that they are normal constituents of the plant.

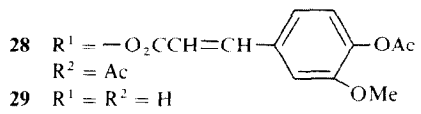
The isolation of a number of biarylheptanoids from *A. japonica* is interesting from a chemotaxonomic viewpoint [8]. In 1966, Erdtman cited the biarylheptanoids as an example of compounds of unique structures which are taxonomically of little utility [10], since at that time biarylheptanoids were known to occur in three unrelated families, Zingiberaceae [11], Leguminosae [12] and Betulaceae [13, 14]. Since then, biarylheptanoids have been isolated from seven species of Betulaceae [8, 9, 15–19] (of which six belong to *Alnus*), two species of Myricaceae [20–23] and one species of Aceraceae [24, 25]. The main occurrence of biarylheptanoids is in the Betulaceae, in three genera, so that they may eventually be of some significance in the chemosystematics of this family. The occurrence of biarylheptanoids in Myricaceae is interesting since this family and the Betulaceae are both in



27 Scheme 1. 26







the Apetalae (Monochlamydeae). The other three families (Aceraceae, Leguminosae and Zingiberaceae) are taxonomically widely separated and comparative studies of the biosynthesis of the biarylheptanoids [26] in such divergent plants would be interesting.

Finally, it is significant that the bridged biarylheptanoids, alnusone (**1**), alnusonol (**2**) and alnusdiol (**5**) co-occur with the corresponding acyclic derivatives, **8**, **7** and **6**. This constitutes the first clear-cut indication of a biosynthetic relationship between these two classes of compound, which has been suggested by many workers [14, 17, 18].

Other phenolic compounds

Of the four phenolics isolated in addition to the biarylheptanoids, three were identified by direct spectroscopic comparison with authentic samples as syringic acid, vanillic acid and 2,6-dimethoxy-1,4-benzoquinone [27]. The remaining compound (**27**) was an optically active phenol, giving a bluish-purple colour with $FeCl_3$. Elementary analysis indicated a molecular formula, $C_{40}H_{42}O_{12}$, and the IR spectrum exhibited absorption bands at 3400 (OH), 1700 (CO), and 1602 and 1505 (aromatic) cm^{-1}. On acetylation, **27** gave the tetraacetate **28**, the NMR spectrum of which showed the presence of four acetoxy groups (6 H singlets at δ 2.13 and 2.28) and four methoxyl groups (6 H singlets at δ 3.75 and 3.88). In conjunction with the facts that a 4 H AB-type quartet with $J = 12$ Hz was observed (δ 6.39 and 7.66), and that part of the aromatic proton signal pattern coincides with those of ferulic acid, it was deduced that **27** was the diferulate ester of a C_{20}-diol, which must contain two phenolic hydroxyl and two methoxyl groups. Thus the C_{20}-diol would be the lignan derived from coniferyl alcohol, most probably secoisolariciresinol (**29**) [28–32]. On this basis the doublet at δ 2.97 ($J = 7$ Hz) and the two double doublets at δ 4.23 and 4.47 ($J = 5$, 12 Hz) in the NMR spectrum of **28** were assigned to the benzyl methylene and the hydroxyl methylene protons, respectively. The remaining β-methine proton signals were assumed to overlap with one of the acetate methyl resonances and this was confirmed by spin decoupling. When the irradiation was made at δ 2.14, the benzyl methylene signal changed to a singlet and the β-methine signal turned to an AB-type quartet. It was concluded, therefore, that **27** was secoisolariciresinol diferulate [33, 34]. This conclusion was verified by alkaline hydrolysis of **27**, which afforded ferulic acid, mp 174°, and secoisolariciresinol (**29**), mp 119–120°, $[\alpha]_D^{16}$ −19.7°.

The isolation of syringic acid and 2,6-dimethoxy-1,4-benzoquinone suggests that air oxidation of the former to the latter could be, at least in some part, responsible for the colour of old stumps of *A. japonica* Steud.

Steroids and triterpenoids

The steroids identified were sitosterol, stigmastanol [35, 36], stigmastanone [37, 38] and sitosteryl D-glucoside [39, 40]. The isolation of stigmastanone from a natural source is unusual. The occurrence of triterpenoids 3-*O*-acetyloleanolic aldehyde [41, 42], erythrodiol 3-acetate [41, 42] and betulinic acid [43] has been confirmed. The former two triterpenes have been isolated from *Machaerium incorruptibile* (Leguminosae) [41] and *Faradaya splendida* (Verbenaceae) [42] and the biogenetic significance of their co-occurrence has been pointed out [41]. The isolation of betulinic acid with taraxerol from the cortex of *A. japonica* has been reported [44, 45]. It is of interest from a chemotaxonomic viewpoint that none of the dammarane-type triterpenoids was found in *A. japonica*, although they have been isolated from several plants of the related *Alnus* species [44–48].

EXPERIMENTAL

All mps are uncorr. Si gel (Merck) was used for column chromatography. IR spectra were recorded as films (liquid) or Nujol mulls (solid), unless otherwise specified. NMR spectra were determined in $CDCl_3$ with TMS as int. standard. Microanalyses were carried out at the Microanalytical Laboratory, Faculty of Science, Osaka City University.

Extraction and isolation. Procedure 1. An 11-yr-old alder tree (*Alnus japonica*) growing by the bank of a marsh in Isono, Yamatotakada-shi, Japan was felled in February and air-dried for 1 year. The shavings (9.75 kg) of the air-dried wood were extracted with boiling MeOH. The MeOH extract was taken up in EtOAc and extracted with satd $NaHCO_3$ (acidic portion, 46 g) followed by 5% NaOH (neutral portion, 38 g; phenolic portion, 38 g). The phenolic portion was chromatographed on a column of Si gel and developed with $CHCl_3$ (fraction (fr.) 1), $CHCl_3$–EtOAc (4:1) (fr. 2) and $CHCl_3$–EtOAc (1:1) (fr. 3). By further chromatographic separations, the following compounds (mg) were obtained from each fraction: fr. 1, **1** (235) and **3** (38); fr. 2, **2** (41) and **6** (20); fr. 3, **5** (7). When the extraction of the green wood was carried out in the same way, the compounds (mg) obtained were: **1** (73); **2** (347); **5** (197). The R_f values of the biarylheptanoid compounds in TLC (Merck pre-coated plates, Si gel 60F-254; C_6H_6–EtOAc, 7:3) were: **1** 0.51; **2** 0.07; **3** 0.47; **5** 0.02; **6** 0.09; **7** 0.14; **8** 0.37.

Procedure 2. The shavings of the green wood (66.1 kg) were extracted with MeOH and the conc extract washed with *n*-hexane. The aq. layer was extracted with EtOAc and the extract (400 g) separated by repeated chromatography on Si gel. The yields of biarylheptanoids were: **1** 316 mg; **7**, 1.85 g; **8**, 81 mg.

Alnusone (**1**). Colourless needles, mp 253–255° (EtOH). Positive $FeCl_3$ test (green colour) only when pyridine was added. UV λ_{max}^{EtOH} nm (log ε): 217 (4.34), 239 (sh, 4.22), 300 (3.58); $\lambda_{max}^{EtOH\ NaOH}$: 218 (4.38), 254 (sh, 4.30), 323 (4.16); IR ν_{max} cm^{-1}:

3300 (OH), 1680 (CO), 1608 (—C=C—), 1505 (aromatic); MS *m/z* (rel. int.): 294 ($M^{+\cdot}$, 39), 276 (8), 251 (7), 233 (7), 225 (51), 211 (100), 197 (18), 183 (41), 165 (55), 115 (65); ^{1}H NMR: δ 2.32–2.92 (6 H, *m*, 3 × CH_2), 2.92–3.24 (2 H, *m*, CH_2), 6.37 (1 H, *d*, *J* = 15.5 Hz, —CH=CHCO—), 6.64–7.12 (7 H, *m*, ArH and —CH_2CH=CHCO—). (Found: C, 77.24; H, 6.18; M^+ 294.1262. $C_{19}H_{18}O$ requires: C, 77.53; H, 6.16%; M, 294.1255).

Dihydroalnusone (**10**). A soln of **1** (20 mg) in EtOH (15 ml) was shaken with H_2 in the presence of 30% Pd on charcoal. Removal of the catalyst and evapn of the solvent from the filtrate gave a crystalline residue which was recrystallized from EtOAc to give colourless leaflets (15 mg), mp 240°. UV λ_{max}^{EtOH} nm (log ε): 248.5 (sh, 3.93), 303 (3.74); IR ν_{max} cm^{-1}: 3300 (OH), 1700 (CO), 1608, 1503 (aromatic); ^{1}H NMR: δ 1.55–2.02 (4 H, *m*, 2 × CH_2), 2.40–2.83 (6 H, *m*, 3 × CH_2), 2.83–3.02 (2 H, *m*, CH_2), 6.47–7.14 (6 H, *m*, ArH).

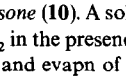
Alnusone diacetate (**9**). A mixture of **1** (40 mg), Ac_2O (0.3 ml) and pyridine (0.3 ml) was left at room temp. overnight. Usual work-up followed by recrystallization of the product from EtOH yielded **9** as colourless leaflets (31 mg), mp 233–236°. UV λ_{max}^{EtOH} nm (log ε): 235 (4.45), 276 (3.96); IR ν_{max} cm^{-1}: 1755 (OAc), 1695 (CO), 1610 (—C=C—), 1225, 1205; MS *m/z* (rel. int.): 378 ($M^{+\cdot}$, 3), 336 (53), 294 (94), 258 (5), 251 (4), 224 (13), 211 (100), 165 (19); ^{1}H NMR: δ 2.16 (6 H, *s*, 2 × OAc), 2.5–3.4 (8 H, *m*, 4 × CH_2), 6.43 (1 H, *d*, *J* = 15.5 Hz, —CH=CH—CHCO), 6.80–7.24 (7 H, *m*, ArH and CH_2CH=CHCO); ^{1}H NMR [0.5 mol equiv. Eu(dpm)$_3$]: 3.52, 3.60 (each 3 H, *s*, OAc), 7.47, 7.60 (each 1 H, *dd*, *J* = 3, 9 Hz, ArH), 8.09 (2 H, *d*, *J* = 9 Hz, ArH), 8.92, 9.06 (each 1 H, *d*, *J* = 3 Hz, ArH). (Found: C, 72.58; H, 5.90. $C_{23}H_{22}O_5$ requires: C, 73.00; H, 5.86%).

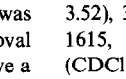
Dihydroalnusone diacetate (**11**). **9** (20 mg) in EtOH (5 ml) was hydrogenated in the presence of Pd on charcoal (10%, 10 mg) to give **11** as colourless leaflets (19 mg), mp 189–191°. UV λ_{max}^{EtOH} nm (log ε): 242 (sh, 4.21), 273 (3.73); IR ν_{max} cm^{-1}: 1755 (OAc), 1702 (CO), 1180, 900; MS *m/z* (rel. int.): 380 ($M^{+\cdot}$, 8), 352 (4), 338 (95), 296 (100), 276 (9), 268 (14), 224 (45), 211 (73), 196 (35), 165 (30), 115 (30). (Found: C, 72.31; H, 6.46. $C_{23}H_{24}O_5$ requires: C, 72.61; H, 6.46%).

Conversion of alnusone diacetate (**9**) *to* **16**. An ice-cooled soln of **8** (68 mg) in HOAc (7 ml) was ozonized and, after addition of H_2O, the mixture was left overnight at room temp. HOAc was removed by steam distillation and the residue extracted with Et_2O. The resultant diacid diacetate (**14**) (48 mg) was hydrolysed by refluxing with aq. 5% KOH. After acidification with 5% HCl, the product was extracted with Et_2O to give the diacid **15** as an oil (40 mg). The oil was dissolved in dry Me_2CO (8 ml) and refluxed with MeI (50 mg) and dry K_2CO_3 (100 mg) for 6 hr. Usual work-up furnished dimethyl 6,6′-dimethoxybiphenyl-3,3′-dipropionate (**16**) as an oil (lit. [4], mp 50.5–53°). **16** was identified by comparison of its IR and NMR spectra and TLC properties with those of an authentic sample.

Alnusonol (**2**). Colourless needles, mp 187–188°, $[\alpha]_D^{16}$ +126.9° (EtOH, *c* 0.51). UV λ_{max}^{EtOH} nm (log ε): 251 (sh, 4.10), 303 (4.03); $\lambda_{max}^{EtOH-NaOH}$ 259 (sh, 4.11), 355 (4.08); IR ν_{max} cm^{-1}: 3410, 3120 (OH), 1700 (CO), 1610, 1582 (aromatic), 1420, 1090, 820 (aromatic); MS *m/z* (rel. int.): 312 ($M^{+\cdot}$ 17), 294 (33), 225 (19), 211 (100), 183 (11), 165 (14), 115 (16); ^{1}H NMR ($CDCl_3$–C_5D_5N): δ 1.76–2.04 (2 H, *m*, CH_2), 2.04–3.36 (8 H, *m*, 4 × CH_2), 4.30 (1 H, *m*, —CH_2CH(OH)CH_2—), 6.62 (2 H, *d*, *J* = 3 Hz, ArH), 6.84 (2 H, *d*, *J* = 8 Hz, ArH), 7.02 (2 H, *dd*, *J* = 3.8 Hz, ArH). (Found: C, 73.51; H, 6.73. $C_{19}H_{20}O_4$ requires: C, 73.06; H, 6.45%).

Acetylation of alnusonol (**2**). **2** (20 mg) was acetylated with Ac_2O–pyridine overnight at room temp. The product was recrystallized from EtOH to afford alnusone diacetate (**9**), mp 233–236° (14 mg), which was identified by its IR and ^{1}H NMR spectra.

Alnusoxide (**3**). This was separated from **1** (which had a similar R_f by repeated chromatography on Si gel columns and prep. TLC with continuous development (C_6H_6–$CHCl_3$, 1:1). Colourless needles (EtOAc), mp 266–269°. UV λ_{max}^{EtOH} nm (log ε): 214 (4.04), 255 (sh, 3.58), 305 (3.43), 340 (3.29); $\lambda_{max}^{EtOH-NaOH}$ 263 (sh, 3.52), 335 (3.73); IR ν_{max}^{KBr} cm^{-1}: 3340, 3040 (OH), 1710 (CO), 1615, 1585 (aromatic), 1230, 1095, 960, 810; ^{1}H NMR ($CDCl_3$–pyridine): δ 1.4–3.7 (10 H, *m*, 4 × CH_2 and ), 6.4–7.1 (6 H, *m*, ArH). (Found: C, 73.25); H, 5.81. $C_{19}H_{18}O_4$ requires: C, 73.53; H, 5.85%).

Alnusoxide diacetate (**4**). **3** was acetylated as described for **2**. Recrystallization of the product from EtOH gave leaflets of **4** (15 mg), mp 213–216°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750 (OAc), 1720 (CO), 1190; MS *m/z* (rel. int.): 394 ($M^{+\cdot}$ 2), 378 (2), 352 (54), 336 (61), 310 (100), 294 (100), 211 (91), 165 (25), 115 (22); ^{1}H NMR: δ 2.20 (6 H, *s*, 2 × OAc), 2.3–3.8 (10 H, *m*, 4 × CH_2 and ), 6.3–7.3 (6 H, *m*, ArH).

Epoxidation of alnusone **1**. To a soln of **1** (55 mg, 0.19 mmol) in MeOH (0.4 ml) was added 6 M NaOH (0.08 ml) followed by 30% H_2O_2 (0.12 ml, 1.2 mmol). The mixture was stirred at 15–20° for 1 hr and at 20–25° for 3 hr. After dilution with H_2O (0.7 ml), the reaction mixture was acidified with 5% H_2SO_4 and extracted with $CHCl_3$. The organic layer was washed with $NaHCO_3$ and satd NaCl soln, and then dried. Evapn of the solvent and recrystallization of the residue furnished alnusoxide (**3**) as needles (26 mg), mp 266–269°. **3** was identified by spectroscopic comparison (^{1}H NMR and IR).

Alnusdiol (**5**). Colourless needles (EtOAc), mp > 300°, $[\alpha]_D^{12°}$ −46.7° (EtOH, *c* 0.52). UV λ_{max}^{EtOH} nm (log ε): 255 (sh, 4.03), 304 (3.95); IR ν_{max} cm^{-1}: 3450, 3280, 3160 (OH), 1618, 1587 (aromatic), 1248, 1230, 1085, 940, 808; ^{1}H NMR (C_5D_5N): δ 1.8–3.5 (10 H, *m*, 5 × CH_2), 4.2–4.6 (2 H, *m*, 2 × CHOH), 7.14 (4 H, *s*, ArH), 7.43 (2 H, *s*, ArH). (Found: C, 72.26; H, 7.20. $C_{19}H_{22}O_4$ requires: C, 72.59; H, 7.05%).

Alnusdiol diacetate (**18**). **5** (27 mg) was acetylated with Ac_2O and pyridine, and the product (**18**) recrystallized from EtOH. Colourless needles, mp 159–162°. IR ν_{max} cm^{-1}: 1768 (ArOAc), 1732 (ROAc), 1250, 1230, 1200, 1180; MS *m/z* (rel. int.): 440 ($M^{+\cdot}$ 53), 398 (78), 338 (13), 278 (39), 260 (47), 211 (30), 43 (100); ^{1}H NMR: δ 1.8–2.2 (2 H, *m*, CH_2), 1.99 (6 H, *s*, 2 × ArOAc), 2.23 (6 H, *s*, 2 × ROAc), 2.4–3.2 (8 H, *m*, 4 × CH_2), 6.95–7.20 (6 H, *m*, ArH). (Found: 66.97; H, 6.30. $C_{27}H_{30}O_8$ requires: C, 67.20; H, 6.27%).

$NaBH_4$ *reduction of alnusonol* (**2**). A soln of **2** (40 mg) in MeOH (3 ml) was made slightly basic (pH 8) by the addition of aq. NaOH, then $NaBH_4$ (33 mg) was added in portions under ice-cooling. The mixture was left to react overnight and was then acidified by the addition of 2 M HCl. After the addition of H_2O (5 ml), the solvent was evapd *in vacuo* and the product extracted with EtOAc. Recrystallization from EtOAc yielded colourless needles of *meso*-alnusdiol (**19**), mp 244–246°, $[\alpha]_D^{14°}$ 0° (EtOH, *c* 0.25). IR ν_{max} cm^{-1}: 3450, 3270 (OH), 1618, 1590 (aromatic), 1250, 1095, 820; ^{1}H NMR ($CDCl_3$–C_5D_5N): δ 1.7–2.2 (6 H, *m*, 3 × CH_2), 2.2–3.0 (4 H, *m*, 2 × CH_2), 4.05–4.36 (2 H, *m*, 2 × CHOH), 6.76–7.08 (6 H, *m*, ArH). (Found: C, 72.59; H, 7.05. $C_{19}H_{22}O_4$ requires: C, 72.26; H, 7.20%).

meso-*Alnusdiol acetate* (**20**). **19** (33 mg) was acetylated with Ac_2O (0.5 ml) and pyridine (0.5 ml) in the usual manner. The product was recrystallized from EtOH to furnish **20** as leaflets (33 mg), mp 181–182°. IR ν_{max} cm^{-1}: 1770 (ArOAc), 1748

(ROAc), 1255, 1230, 1208, 1052. (Found: C, 67.00; H, 6.40. $C_{27}H_{30}O_8$ requires: C, 67.20; H, 6.27%).

$LiAlH_4$ *reduction of alnusonol* (**2**). To a suspension of $LiAlH_4$ (38 mg, 1.0 mmol) in dry THF (2 ml) was added dropwise a soln of **2** (40 mg, 0.13 mmol) in dry THF (2 ml) under ice-cooling and stirring. The mixture was refluxed for 2 hr and then the excess reagent was destroyed by the addition of EtOH. 2M HCl (1 ml) and H_2O (2 ml) were added and the product was extracted with EtOAc (× 3). The organic layer was washed with $NaHCO_3$ soln, dried and the solvent evapd. The oily residue (38 mg) was separated by prep. TLC with continuous development using C_6H_6–EtOAc (2:3). The product with the higher R_f had a mp of 244–256° (5 mg, EtOAc) and was identified as *meso*-alnusdiol (**19**). The product with the lower R_f, mp 300° (10 mg, EtOAc) was identical with the authentic specimen of alnusdiol (**5**).

Hannokinol (**6**). This compound was isolated from the fraction containing **5** by prep. TLC with continuous development ($CHCl_3$–EtOAc, 3:2). Colourless plates, mp 154–156° (C_6H_6–Me_2CO, 1:1) (lit. [8] 165–166°). UV λ_{max}^{EtOH} nm (log ε): 203 (4.53), 226 (4.23), 280.5 (3.58); $\lambda_{max}^{EtOH-NaOH}$ 228 (4.19), 243 (4.22), 289 (3.64), 298 (3.64); IR ν_{max} cm^{-1}: 3430, 3260 (OH), 1617, 1605 (aromatic), 1245, 820; MS *m/z* (rel. int.): 316 ($M^{+\cdot}$, 5), 298 (11), 280 (11), 160 (21), 149 (10), 133 (14), 120 (14), 107 (100); ^1H NMR ($CDCl_3$–C_5D_5N): δ 1.48–1.96 (6 H, *m*, 3 × CH_2), 2.68 (4 H, *m*, 2 × CH_2Ar), 4.04 (2 H, *m*, CHOH), 6.80, 7.00 (8 H, AB*q*, *J* = 8 Hz, ArH). Upon acetylation **6** afforded the tetraacetate **22** as an oil. ^1H NMR: δ 1.55–1.98 (6 H, *m*, 3 × CH_2), 1.98 (6 H, *s*, 2 × ROAc), 2.26 (6 H, s, 2 × ArOAc), 2.60 (2 H, *t*, *J* = 8 Hz, $ArCH_2CH_2$), 4.98 (2 H, *quintet*, *J* = 6 Hz, $CH_2CHOHCH_2$), 6.95, 7.14 (8 H, AB *q*, *J* = 8 Hz, ArH). **6** was identified as 1,7-bis[4-hydroxyphenyl]heptan-3,5-diol (hannokinol) by comparison of its IR and ^1H NMR spectra with those of an authentic specimen provided by Professor Sasatani [8].

Hannokinin (**7**). Colourless needles, mp 139–140° (C_6H_6–Me_2CO, 1:1) (lit. [8] 131–132°). IR ν_{max} cm^{-1}: 3440, 3320, 3180, 1695 (CO), 1612, 1595 (aromatic), 1230, 1037, 820; ^1H NMR (CD_3OD): δ 1.64 (2 H, *q*, *J* = 8 Hz, CH_2CH_2CHOH), 2.20–2.72 (8 H, *m*, 4 × CH_2), 3.98 (1 H, *quintet*, *J* = 6 Hz, $CH_2CHOHCH_2$), 6.67, 6.98 (8 H, AB*q*, *J* = 8 Hz, ArH). The IR spectrum was superimposable on that of authentic hannokinin.

$NaBH_4$ *reduction of hannokinin* (**7**). $NaBH_4$ (100 mg) was added in portions to an ice-cooled and stirred soln of **7** (100 mg) in MeOH (9 ml) over 20 min. The mixture was then left at room temp. overnight. 2 M HCl (3 ml) and H_2O (20 ml) were added and the MeOH was evapd *in vacuo*. The residue was extracted with EtOAc (20 ml × 4), washed with H_2O and then dried. The diastereomeric mixture, obtained after the evapn of the solvent, was separated by continuous development TLC (C_6H_6–EtOAc, 3:4). The separated products were recrystallized from C_6H_6–Me_2CO (1:1). The product with the lower R_f (mp 154–156°, 11 mg) was identified as hannokinol (**6**). The other product (12 mg), mp 139–141°, was assigned the *meso*-structure (**23**). IR ν_{max} cm^{-1}: 3460, 3320 (OH), 1623, 1610 (aromatic), 1240, 1180, 830. ^1H NMR ($CDCl_3$–C_5D_5N): δ 1.50–1.95 (6 H, *m*, 3 × CH_2), 2.46–2.84 (4 H, *m*, 4 × $ArCH_2$), 3.90 (2 H, *quintet*, $CH_2CH(OH)CH_2$), 6.77, 6.98 (8 H, AB*q*, *J* = 8 Hz, ArH). (Found: C, 71.97; H, 7.58. $C_{19}H_{24}O_4$ requires: C, 72.12; H, 7.65%).

1,7-*Bis*[4-*hydroxyphenyl*]-3-*hepten*-5-*one* (**8**). This compound was obtained as a colourless, viscous oil. IR ν_{max} cm^{-1}: 3360 (OH), 1685 (CO), 1658 (—C=C—), 1620, 1608, 1240, 830; ^1H NMR ($CDCl_3$–CD_3OD): δ 2.48 (2 H, *t*, *J* = 7 Hz, $COCH_2CH_2Ar$), 2.66 (2 H, *t*, *J* = 7 Hz, $COCH_2CH_2Ar$), 2.77 (4 H, *s*, $ArCH_2CH_2CH$=), 6.03 (1 H, *dt*, *J* = 16, 3 Hz, CH_2CH=$CHCO$), 6.80 (1 H, *dt*, *J* = 16, 7 Hz, CH_2CH=$CHCO$), 6.72, 6.96 (8 H, AB*q*, *J* = 8 Hz, ArH). The diacetate (**24**) of **8** was prepared in the usual manner. ^1H NMR: δ 2.28 (6 H, *s*, 2 × OAc), 2.53 (2 H, *t*, *J* = 7 Hz, $COCH_2CH_2Ar$), 2.75 (2 H, *t*, *J* = 7 Hz, $COCH_2CH_2Ar$), 2.86 (4 H, *s*, $ArCH_2CH_2CH$=), 6.08 (1 H, *dt*, *J* = 16, 3 Hz, CH=CHCO), 6.82 (1 H, *dt*, *J* = 16, 7 Hz, CH_2CH=$CHCO$), 6.97, 7.17 (4 H, AB*q*, *J* = 8 Hz, ArH), 6.99, 7.19 (4 H, AB*q*, *J* = 8 Hz, ArH).

1,7-*Bis*[4-*methoxyphenyl*]-3-*hepten*-5-*one* (**25**). **8** (43 mg) was treated with dry Me_2CO (8 ml), MeI (50 mg) and dry K_2CO_3 (80 mg) under reflux for 7 hr. The inorganic salt was removed by filtration and the filtrate was evapd to leave a crystalline residue, which was recrystallized from *iso*-PrOH. The diMe ether **25** was obtained as colourless plates (28 mg), mp 50–51°. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1703, 1680 (CO), 1630 (—C=C—), 1615, 1590, 1512 (aromatic), 1247, 1175, 1040; ^1H NMR (CCl_4): δ 2.41 (2 H, *t*, *J* = 7 Hz, $COCH_2CH_2Ar$), 2.52–2.88 (6 H, *m*, 3 × CH_2), 3.66 (6 H, *s*, 2 × Me), 5.90 (1 H, *dt*, *J* = 16, 3 Hz, $COCH$=$CHCH_2$), 6.64 (1 H, *dt*, *J* = 16, 7 Hz, $COCH$=$CHCH_2$), 6.61, 6.90 (4 H, AB*q*, *J* = 8 Hz, ArH), 6.63, 6.92 (4 H, AB*q*, *J* = 8 Hz, ArH).

Synthesis of 1,7-*bis*[4-*methoxyphenyl*]-3-*hepten*-5-*one* (**25**). (a) 3-[4-Methoxyphenyl]propanal (**26**). A soln of 3-[4-methoxyphenyl]propan-1-ol (3.5 g, 21 mmol) in CH_2Cl_2 (35 ml) was added to a soln of Collins' reagent (prepared *in situ* [50] from CrO_3, 10.7 g, 107 mmol; pyridine, 16.9 g and CH_2Cl_2, 268 ml) and the mixture was allowed to react for 15 min. The decanted soln and the Et_2O washings of the residue were combined, and washed successively with dil HCl (× 3), satd $NaHCO_3$ and satd NaCl soln, then dried. Evapn of the solvent left an oily residue (3.082 g) which was purified by Si gel chromatography to give **26** as an oil (2.084 g).

(b) 3-[4-Methoxyphenyl]propionylmethylenetriphenylphosphorane (**27**). A mixture of 3-[4-methoxyphenyl]propionic acid (3.06 g, 17 mmol), $SOCl_2$ (3.18 g, 25.5 mmol) and C_6H_6 (10 ml) was refluxed for 1 hr. The solvent and the excess of the reagent were evapd *in vacuo*. The acid chloride obtained (3.457 g) was dissolved in dry Et_2O (70 ml) and added dropwise to a soln of methylenetriphenylphosphorane (prepared from methylenetriphenylphosphonium bromide, 12.14 g, 34 mmol and 1.6 M *n*-BuLi soln in hexane, 22.5 ml, 36 mmol [51]). The mixture was stirred for 30 min and then the solvent was evapd. The residue was extracted with EtOAc and the extract was dried then evapd. The brown-coloured oil (3.617 g) was recrystallized from EtOAc, giving the ylide **27** as pale yellow leaflets, mp 143–145° (1.456 g).

(c) Reaction between **26** and **27**. A mixture of the aldehyde **26** (814 mg, 2 mmol) and the ylide **27** (328 mg, 2 mmol) in dry toluene (13 ml) was refluxed for 30 hr. The solvent was evapd and the residue was triturated with a mixture of Et_2O and petrol. The extract (647 mg) was chromatographed on a column of Si gel (13 g) to give crystalline fractions, which were recrystallized from *iso*-PrOH. Crystals, mp 50–51°. It was identical with methyl ether **25** described above. (Found: C, 77.58; H, 7.46. $C_{21}H_{24}O_3$ requires: C, 77.75; H, 7.46%).

Vanillic acid (*mp* 213–215°, EtOAc) *and syringic acid* (*mp* 201–202°, EtOAc). These had IR spectra which were indistinguishable from authentic specimens.

2,6-*Dimethoxy*-1,4-*benzoquinone*. Orange yellow needles, mp 239–242°. IR ν_{max}^{Nujol} cm^{-1}: 3075, 1700, 1645, 1600, 1325, 1260, 1225, 1115, 1010, 880. ^1H NMR ($CDCl_3$–C_5D_5N): δ 3.65 (6 H, *s*, 2 × OMe), 5.77 (2 H, *s*). (Found: C, 56.58; H, 4.79. Calc. for $C_8H_8O_4$: C, 57.14; H, 4.08%). The authentic sample was prepared by HNO_3 oxidation of pyrogallol trimethyl ether [52, 53].

Secoisolariciresinol diferulate (**27**). Colourless needles (EtOAc), mp 204–205°, $[\alpha]_D^{16}$ −52.5° (pyridine, *c* 0.65). IR

ν_{max}^{Nujol} cm^{-1}: 3400, 1700, 1602, 1505, 1240, 1025. (Found: C, 67.21; H, 6.00. $C_{40}H_{42}O_{12}$ requires: C, 67.21; H, 5.92%).

Tetraacetate of **27** (**28**). The acetylation of **27** (200 mg) with Ac_2O and pyridine at room temp. furnished the tetraacetate **28** as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1710, 1630, 1600, 1250, 1150, 1120, 1035, 1010, 980, 900, 845, 828; ^{1}H NMR ($CDCl_3$): δ 2.14, 2.28 (each 6 H, *s*, 4 × OAc), 2.97 (4 H, *d*, J = 7 Hz, ArC$\underline{H}_2$CH—), 3.75, 3.88 (each 6 H, *s*, 4 × OMe), 4.23, 4.47 (each 2 H, *dd*, J = 5, 12 Hz, —CHC$\underline{H}_2$OR), 6.39 (2 H, *d*, J = 12 Hz, ArCH=C$\underline{H}$CO$_2$—), 6.65–7.38 (12 H, *m*, ArH), 7.66 (2 H, *d*, J = 12 Hz ArC$\underline{H}$=CHCO$_2$—).

Hydrolysis of **28**. **28** (200 mg) in EtOH (29 ml) and 2 M NaOH (20 ml) was refluxed for 2 hr. After cooling, CO_2 gas was bubbled through the reaction mixture and the resulting ppt. was collected by filtration. Recrystallization afforded secoisolariciresinol (**29**) as colourless plates, mp 119–120° (lit. [28], 112.5–113.5°), $[\alpha]_D$ − 19.7° (pyridine, *c* 0.89), (lit. [28], $[\alpha]_D$ − 35.6° (Me_2CO, *c* 1.07)). IR ν_{max}^{Nujol} cm^{-1}: 3440, 3130, 1610, 1518, 1272, 1158, 1040, 843, 800. (Found: C, 66.00; H, 7.25. Calc. for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23%). The IR spectrum was identical with that of an authentic sample kindly provided by Professor Sakakibara [31]. The acidic product was isolated after acidification of the filtrate and Et_2O extraction. Mp 174° (Et_2O). The IR spectrum was superimposable on that of authentic ferulic acid.

Sitosterol. Needles, mp 143–144° (EtOH), $[\alpha]_D^{17}$ −29.5° ($CHCl_3$, *c* 0.65), [lit. [54]), mp 137.5–138°, $[\alpha]_D$ −34.34° ($CHCl_3$, *c* 1.03)]. The IR spectrum was identical with that of an authentic sample prepared by hydrogenation of stigmasterol (Pd–C) [55]. Acetate, mp 123–124° (lit. [54], mp 127–129°).

Stigmastanol. Needles, mp 136–139° (EtOH). MS *m/z*: 416.4009 ($M^{+\cdot}$, $C_{29}H_{52}O$ = 416.4016). This compound was identical with the product obtained from stigmasterol by catalytic hydrogenation (Pd–C/H_2 and then PtO_2/H_2 [54]).

Stigmastanone. Needles, mp 157–160° (EtOH) (lit. [37], mp 157–159°). This compound was identical with the product obtained by Jones' oxidation of stigmastanol.

Sitosteryl D-*glucoside.* Needles, mp 299–303° (EtOH), (lit. [40] mp 290–291°). On acetylation with Ac_2O–pyridine, a tetraacetate was obtained, needles, mp 171–173° (EtOH). (Found: C, 69.35; H, 9.14. Calc. for $C_{43}H_{68}O_{10}$: C, 69.32; H, 9.20%). The IR spectra of both were identical to those reported in the literature [40]. When the tetraacetate (68 mg) was hydrolysed by heating with dioxane (7 ml) and 1 M H_2SO_4 (7 ml) for 10 hr, sitosterol was obtained.

3-O-*Acetyloleanolic aldehyde.* Needles, mp 216–218°(EtOH), (lit. [41], 225–226°). IR ν_{max}^{Nujol} cm^{-1}: 2740, 1735, 1250, 1025, 993. MS *m/z* (rel. int.): 452 (9), 422 (10), 407 (14), 393 (10), 392 (8), 379 (8), 253 (10), 239 (80), 211 (100), 210 (90), 195 (99), 181 (55), 109 (60); ^{1}H NMR ($CDCl_3$): δ 0.73 (3 H, *s*, Me), 0.86 (6 H, 2 × Me), 0.93 (6 H, *s*, 2 × Me), 0.95 (3 H, *s*, Me), 1.14 (3 H, *s*, Me), 2.03 (3 H, *s*, OAc), 2.64 (1 H, *br. dd*, J = 5, 14 Hz, —CHC$\underline{H}_2$CH=), 4.48 (1 H, *dd*, J = 7.5, 9 Hz, —C$\underline{H}$(OAc)CH$_2$—), 5.32 (1 H, *t*, J = 4 Hz, —C=C$\underline{H}$CH$_2$—), 9.40 (1 H, *s*, —CHO). (Found: C, 79.31; H, 1.05. Calc. for $C_{32}H_{50}O_3$: C, 79.62; H, 10.51%). When this compound (11.9 mg) in MeOH was treated with $NaBH_4$ (2 mg) for 0.5 hr, a product was obtained which was identified as erythrodiol by comparison of its IR spectrum with that of an authentic sample sent by Professor I. Kitagawa (Osaka University, Faculty of Pharmaceutical Sciences).

Erythrodiol 3-acetate. Needles, mp 243–244° (EtOH), (lit. [41], 237–239°). IR ν_{max}^{Nujol} cm^{-1}: 3480 (OH), 1712 (CO), 1265, 1045, 1025, 1005; MS *m/z*: 466.3773 ($M^{+\cdot}$, $C_{32}H_{50}O_2$ = 466.3809); ^{1}H NMR ($CDCl_3$): δ 0.89 (12 H, *s*, 4 × Me), 0.96 (6 H, *s*, 2 × Me), 1.17 (3 H, *s*, Me), 2.06 (3 H, *s*, Me), 3.21, 3.51 (each 1 H, AB*q*, J = 12 Hz, C$\underline{H}_2$OH), 4.50 (1 H, *dd*, J = 7, 10 Hz, —C$\underline{H}$(OAc)CH$_2$—), 5.19 (1 H, *t*, J = 3.5 Hz, —C=C$\underline{H}$CH$_2$—). ^{13}C NMR ($CDCl_3$)*: δ 15.7 (*q*, C-25), 16.9 (*q*, C-26), 16.9 (*q*, C-24), 18.4 (*t*, C-6), 21.4 (*q*, acetyl methyl), 22.2 (*t*, C-16), 23.7 (*q*, C-30), 23.7 (*t*, C-11), 23.7 (*t*, C-2), 25.7 (*t*, C-15), 26.1 (*q*, C-27), 28.2 (*q*, C-23), 31.2 (*s*, C-20), 31.1 (*t*, C-22), 32.7 (*t*, C-7), 33.3 (*q*, C-29), 34.3 (*t*, C-21), 37.0 (*s*, C-10), 37.0 (*s*, C-8), 37.1 (*s*, C-4), 37.9 (*s*, C-1), 38.5 (*t*, C-17), 41.9 (*s*, C-14), 42.5 (*d*, C-18), 46.6 (*t*, C-19), 47.7 (*d*, C-9), 55.4 (*d*, C-5), 69.8 (*t*, C-28), 81.0 (*d*, C-3), 122.4 (*d*, C-12), 144.4 (*s*, C-13), 171.0 (*s*, acetyl carbonyl). (Found: C, 79.26; H, 10.96. Calc. for $C_{32}H_{52}O_3$: C, 79.28; H, 10.81%). Acetylation in the usual way (Ac_2O–pyridine) yielded erythrodiol diacetate, mp 191–193° (lit. [58], 188°). IR ν_{max}^{Nujol} cm^{-1}: 1735 (OAc), 1245, 1230, 1145, 1020; ^{1}H NMR ($CDCl_3$): δ 0.90 (12 H, *s*, 4 × Me), 0.97 (6 H, *s*, 2 × Me), 1.18 (3 H, *s*, Me), 2.06 (6 H, *s*, 2 × OAc), 3.72, 4.05 (each 1 H, AB*q*, J = 12 Hz, CH_2OAc), 4.51 (1 H, *dd*, J = 8, 9 Hz, —CH(OAc)CH$_2$—), 5.21 (1 H, *t*, J = 3.5 Hz, —C=C$\underline{H}$CH$_2$—). (Found: C, 77.62; H, 10.41. Calc. $C_{34}H_{54}O_4$: C, 77.52; 10.33%). Final identification was performed by alkaline hydrolysis, which afforded erythrodiol (IR comparison).

Betulinic acid. Needles, mp 298–301° (EtOH), (lit. [43], 313.5–316.5°). IR ν_{max}^{Nujol} cm^{-1}: 3420 (OH), 3080 (CH_2), 1695 (CO), 1645 (CH_2), 1280, 1048, 1035, 885 (=CH_2): ^{1}H NMR ($CDCl_3$–pyridine): δ 0.83, 0.90, 1.01, 1.03, 1.38 (each 3 H, *s*, Me), 1.75 (3 H, *s*, —C(C$\underline{H}_3$)=CH$_2$), 2.49 (1 H, *d*(*br*), C-19 methine), 3.51 (1 H, *dd*, J = 8, 10 Hz, —CH$_2$C$\underline{H}$(OH)—), 4.65, 4.81 (each 1 H, *s*(*br.*), =CH_2). Acetylation (Ac_2O pyridine) afforded the corresponding acetate, mp 263–265° (EtOH), (lit. [56], 288–290°). IR ν_{max}^{Nujol} cm^{-1}: 3060 (=CH_2), 1740 (OAc), 1695 (CO_2H), 1638 (=CH_2), 1240, 1020, 975, 880; ^{1}H NMR ($CDCl_3$): δ 0.85 (9 H, *s*, 3 × Me), 0.95, 0.98 (each 3 H, *s*, Me), 1.70 (3 H, *s*, —C(C$\underline{H}_3$)=CH$_2$), 4.48 (1 H, *dd*, J = 8, 9 Hz, —C$\underline{H}$(OAc)CH$_2$), 4.62, 4.74 (each 1 H, *s*(*br.*), =CH_2); MS *m/z* (rel. int.): 498.3697 ($M^{+\cdot}$, 11; $C_{32}H_{50}O_4$, 498.3707), 466 (33), 438 (38), 423 (17), 395 (15), 189 (100). Methylation (CH_2N_2) gave the corresponding Me ester, mp 222–235° (EtOH), (lit. [43], 224–225°). IR ν_{max}^{Nujol} cm^{-1}: 3550 (OH), 3080 (=CH_2), 1720 (CO_2Me), 1640 (=CH_2), 1200, 1165, 1050, 885 (=CH_2); ^{1}H NMR ($CDCl_3$): δ 0.78, 0.84, 0.94 (each 3 H, Me), 0.88 (6 H, *s*, 2 × Me), 1.75 (3 H, *s*, —C(C$\underline{H}_3$)=CH$_2$), 3.12 (1 H, *m*, —CH(OH)CH$_2$—), 3.75 (3 H, *s*, CO_2CH_3), 4.65, 4.80 (each 1 H, *s*(*br.*), =CH_2).

* The assignments were made with the aid of off-resonance spectrum (multiplicity in parentheses) and by reference to the data of closely related compounds [57].

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