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TRITERPENOIDS—LIV

THE CONSTITUTION OF ALNUSENONE

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Abstract—The constitution and stereochemistry of alnusenone have been established and a partial synthesis of alnusenone (II) from friedelin is described. Taraxerone (I) and alnusenone (II) probably represent stabilised intermediates in the biogenesis of friedelin (XV) from squalene.

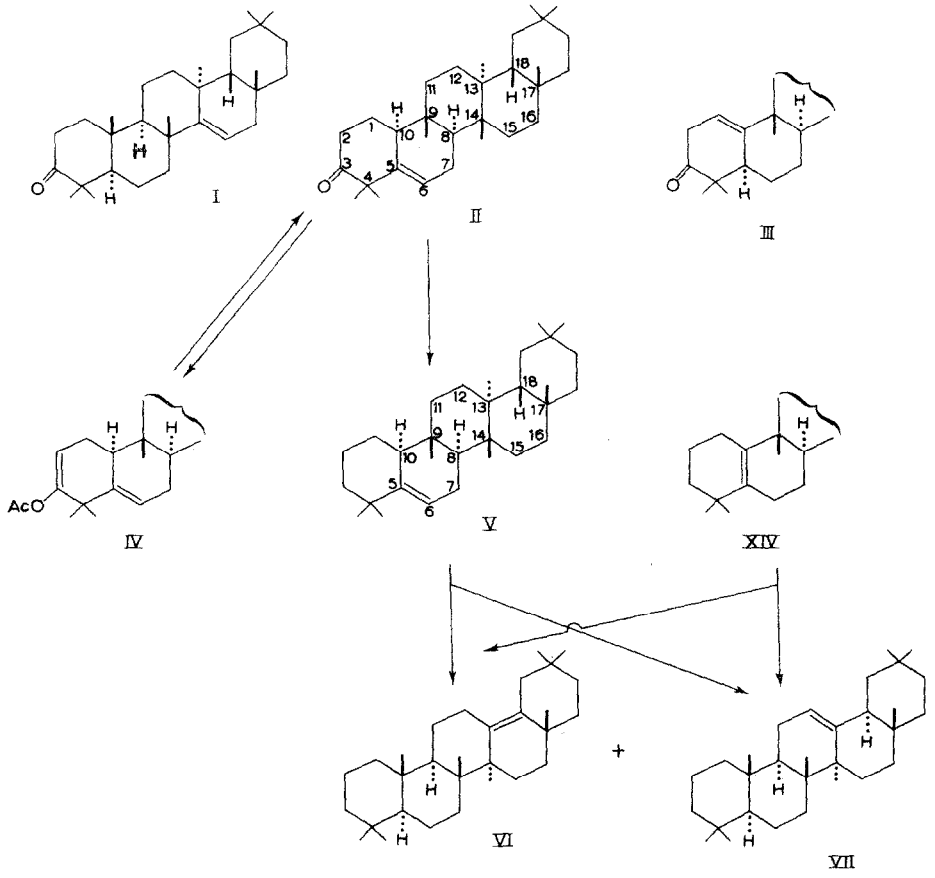
THE unsaturated pentacyclic ketone alnusenone accompanies the isomeric taraxerone in the unsaponifiable matter from alder bark.[1,2,3] The carbonyl group in alnusenone is not hindered since the ketone forms an oxime[3] and on reduction with either lithium aluminium hydride[1,3] or sodium and alcohol[3] it gives a secondary alcohol, alnusenol, which readily forms esters and which is reconverted into alnusenone on oxidation.[3] We consider that the hydroxyl group in alnusenol is equatorial because the alcohol is recovered in high yield after prolonged treatment with sodium amyloxide in air at 170°.

The ethylenic bond in alnusenone is not conjugated with the carbonyl group since alnusenone does not show the characteristic ultra-violet and infra-red absorption spectra of an $\alpha\beta$-unsaturated ketone[3,4] and it is unhindered because alnusenyl acetate is easily reduced to the saturated alnusanyl acetate;[3] alnusenyl acetate readily gives an epoxide on oxidation with monoperphthalic acid. An indication that the ethylenic bond in alnusenone is trisubstituted was afforded by the intensity of short wavelength ultra-violet absorption of alnusenyl acetate[3] and by the infra-red absorption spectrum of the acetate (in carbon disulphide) which includes a band at 788 cm^{-1}. The trisubstituted nature of the double bond in alnusenyl acetate is supported by the following observations. Oxidation of the acetate with osmic acid followed by acetylation gives a saturated triol diacetate which is stable to chromic-acetic acid mixture at room temperature.

As stated above, alnusenone occurs in alder bark associated with the isomeric taraxerone (I) and mixtures of the two ketones are difficult to seperate. These facts led us to make two assumptions which guided further experiment and, in the event, transpired to be justified. First, we assumed a biogenetic relationship between alnusenone and taraxerone and secondly, we assumed that the carbonyl group in alnusenone is at position 3 in an oleanane or modified oleanane carbocyclic structure. The validity of the first assumption was established by the discovery that the hydrocarbon alnusene,[3,4] obtained from alnusenone by the Wolff–Kishner method, is isomerised by mineral acid to a crystal mixture of olean-13(18)-ene (VI) and 18α-olean-12-ene (VII) identical with the hydrocarbon mixture obtained by similar treatment of olean-12-ene (β-amyrene), olean-13(18)-ene, olean-18-ene (germanicene) and friedelene.[5]

[1] S. Chapon and S. David *Bull. Soc. Chim. Fr.* 333 (1953).
[2] S. Chapon and S. David *C.R. Acad. Sci., Paris* **238**, 1600 (1954).
[3] J. M. Beaton, F. S. Spring and R. Stevenson *J. Chem. Soc.* 2616 (1955).
[4] S. Chapon *Bull. Soc. Chim. Fr.* 1076, 1630 (1955).
[5] G. Brownlie, M. B. E. Fayez, F. S. Spring, R. Stevenson and W. S. Strachan *J. Chem. Soc.* 1377 (1956).

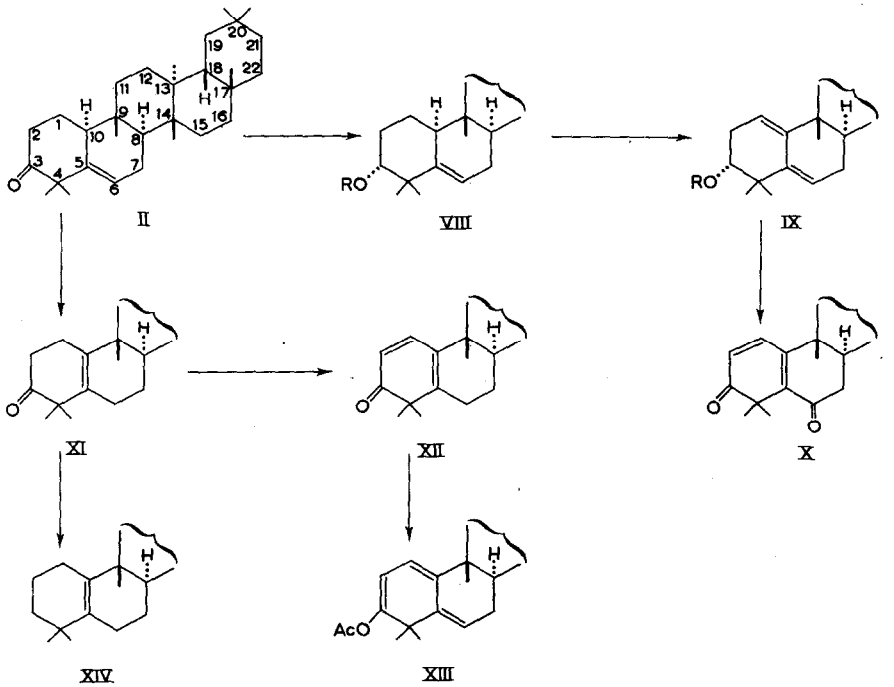
Further information concerning the immediate environment of the trisubstituted double bond in alnusenone was obtained from a consideration of the behaviour of alnusenyl acetate with selenium dioxide. The product of this reaction is an alnusadienyl acetate, the ultra-violet absorption spectrum of which shows it to contain a hetero-annular diene system.[4] Partial catalytic reduction of alnusadienyl acetate gives alnusenyl acetate and complete reduction gives alnusanyl acetate, so establishing that the formation of alnusadienyl acetate from alnusenyl acetate does not involve a molecular rearrangement.



At an early stage of this study a difference was noted between the intensity of the short wavelength ultra-violet absorption of alnusenyl acetate which, as stated earlier, is typical of a trisubstituted double bond and that of alnusenone. In the spectrum of alnusenyl acetate there is a rapid fall in intensity between 2100 and 2300 Å whereas there is a much less marked intensity decrease for alnusenone. This we attribute to a close proximity of the carbonyl group and double bond in alnusenone.

	ε at					
	2050	2100	2150	2200	2300	2400 Å
Alnusenone	3500	2600	1700	1200	400	0
Alnusenyl acetate	3300	2300	950	0	0	0

Assuming that the carbonyl oxygen in alnusenone is attached to C_3 the considerations discussed above lead to the view that the ketone is either (II) or (III). Of these the latter is excluded and the former is supported by the following facts. Alnusenone is not isomerised to an $\alpha\beta$-unsaturated ketone by either alkali or mineral acid. Treatment of alnusenone with *iso*propenyl acetate gives an enol acetate which does not contain a conjugated diene system since it does not show high intensity absorption in the ultra-violet region above 2200 Å; alkaline hydrolysis of the enol acetate regenerates alnusenone. Moreover pyrolysis of alnusenyl benzoate gives a hydrocarbon which is not a conjugated diene since it does not show high intensity absorption above 2200 Å. Alnusenone is therefore formulated as (II) (alnus-5-en-3-one) and the enol acetate as (IV). The hydrocarbon obtained by Wolff–Kishner reduction of alnusenone is alnus-5-ene (V) and the mineral acid isomerisation of this hydrocarbon is represented as a "back-bone" rearrangement induced by protonation of the 5:6-double bond followed by migration of the axial groups or atoms attached to C_{10}, C_9, C_8, C_{14}, and C_{13} to C_5, C_{10}, C_9, C_8, and C_{14} respectively and elimination of a proton from C_{12} and/or C_{18} to give olean-12-ene and/or olean-13(18)-ene. Either of these hydrocarbons is known[5] to give an equilibrium mixture of olean-13(18)-ene (VI) and 18α-olean-12-ene (VII) when treated with mineral acid. Since the hydroxyl group in alnusenol is equatorial we represent this alcohol as alnus-5-en-3α-ol (VIII) and alnusadienyl acetate as alnusa-1(10):5-dien-3α-yl acetate (IX; R = Ac).



Evidence supporting the view that alnusenone is (II) was obtained as follows. Hydrolysis of alnusa-1(10):5-dien-3α-yl acetate using lithium aluminium hydride gives alnusa-1(10):5-dien-3α-ol (IX; R = H) which, like the parent acetate, exhibits the ultra-violet absorption spectrum of a conjugated heteroannular diene with a principal maximum at 2390 Å (ε = 17,000) and subsidiary maxima at 2320 and 2480 Å.

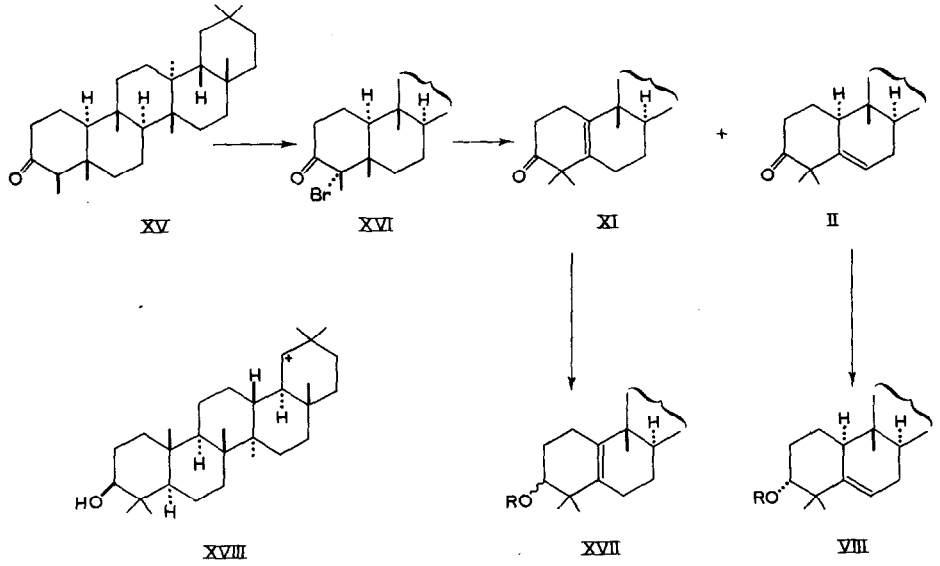
In an attempt to prepare the ketone corresponding to the 1(10):5-dienol, which, it was anticipated, should readily isomerise to a fully conjugated dienone, the dienol was oxidised with chromic acid-pyridine complex at room temperature. The product of the reaction, however, is a yellow-coloured compound, $C_{30}H_{44}O_2$, the ultra-violet absorption spectrum of which shows maxima at 2180 ($\varepsilon = 11{,}000$) and 3190 Å ($\varepsilon = 8300$) and we represent this compound as alnusa-1:5(10)-diene-3:6-dione (X). The dienyl acetate (IX; R = Ac) is not oxidised by chromic acid-pyridine complex at room temperature.

We now turn to a consideration of the behaviour of alnusenone with mineral acid. Chapon[4] converted alnusenone into an isomeric "ketone-II" by relatively mild treatment with sulphuric–acetic acid mixture. Wolff–Kishner reduction of "ketone-II" gave the "hydrocarbon-II" and reduction of "ketone-II" with lithium aluminium hydride gave "alcohol-II" which was characterised by the formation of its acetate. We have obtained "ketone-II" by treatment of alnusenone with hydrochloric–acetic acid mixture, and from this ketone the related "alcohol-II" and its acetate were prepared. The constants of the last two compounds differ appreciably from those previously reported.[4] The infra-red absorption spectrum of the "acetate-II" confirms the view[4] that its double bond is fully substituted. The double bond in "ketone-II" is still in the near neighbourhood of the carbonyl group since successive treatment of "ketone-II" with bromine and potassium acetate yields a compound, $C_{30}H_{46}O$, the absorption spectrum of which shows a maximum at 3220 Å indicating the presence of a fully conjugated dienone chromophore. The infra-red absorption spectrum (in Nujol) of the dienone $C_{30}H_{46}O$, includes a strong carbonyl band at 1670 cm^{-1}. Accordingly we represent "ketone-II" as alnus-5(10)-en-3-one (XI), and the conjugated dienone as alnusa-1:5 (10)-dien-3-one (XII). Treatment of alnusa-1:5(10)-dien-3-one with *iso*propenyl acetate gives an enol acetate (XIII) the ultra-violet absorption spectrum of which includes a band at 3160 Å ($\varepsilon = 9100$). "Hydrocarbon-II" obtained by Wolff–Kishner reduction of alnus-5(10)-en-3-one is alnus-5(10)-ene (XIV) and like alnus-5-ene (V) it is smoothly isomerised to a mixture of olean-13(18)-ene (VI) and 18α-olean-12-ene (VII) when treated with hydrochloric-acetic acid.

Treatment of alnus-5(10)-en-3-one (XI) with mineral acid, using conditions which convert alnus-5(10)-ene into the mixture of olean-13(18)-ene and 18α-olean-12-ene, gives a complex mixture which does not contain any appreciable quantity of olean-13 (18)-en-3-one. We attribute the difference in behaviour towards mineral acid between alnusene and alnusenone to the proximity of the ethylenic bond and the carbonyl group in the latter.

Chapon and David[2] have reported that treatment of the new pentacyclic ketone from alder bark with osmic acid in chloroform gives taraxerone in a yield which, although variable, is never less than 28 per cent. The French authors were aware that the former ketone is very difficult to separate from taraxerone and were at pains to ensure that the specimen employed for this reaction was homogeneous. They also report that a similar isomerisation was observed by treatment of alnusenyl acetate with osmic acid, presumably giving taraxeryl acetate. We have not been able to repeat these isomerisations and, as stated earlier, we find that treatment of alnusenyl acetate with osmic acid followed by acetylation gave a saturated triol diacetate together with unchanged alnusenyl acetate. If the view, which is discussed later, that the C_{10}-hydrogen atom in alnusenone is α-orientated is correct it follows that the equatorial

hydroxyl group in alnusenol is also α-orientated in which case the mechanism whereby alnusenyl acetate is converted into taraxeryl acetate, a 3β-acetate, is obscure.*



The derivation of the structure (II) for alnusenone connotes a close relationship between this compound and friedelin (XV), the saturated pentacyclic ketone isolated from cork.[6,7] In a preliminary communication Corey and Ursprung[7] described the formation of 4-bromofriedelin (XVI) by the action of bromine on friedelin enol benzoate and they showed that the bromine atom in 4-bromofriedelin is axial. The position of the bromine atom in 4-bromofriedelin was deduced from its reaction with silver acetate which gives an unsaturated ketone, m.p. 247–248°, $[\alpha]_D$ — 48·6° which "is not isomerised to a conjugated structure" and which was formulated as (II), i.e. the structure now proposed for alnusenone. We have again prepared the unsaturated ketone from 4-bromofriedelin but we find, however, that this reaction product is a mixture since, on reduction with lithium aluminium hydride followed by acetylation, it gives a mixture of alnusenyl acetate (VIII, R = Ac) and alnus-5(10)-enyl acetate (XVII, R = Ac) which is readily separated into its components by crystallisation. Furthermore, crystallisation of a mixture of two parts of alnus-5(10)-en-3-one (m.p. 250–252°, $[\alpha]_D$ — 90°) (XI) and one part of alnusenone (m.p. 245–246°, $[\alpha]_D$ + 31°) (II) gave a ketone mixture, m.p. 247–249°, $[\alpha]_D$ — 51° which is identical with the product (m.p. 247–249°, $[\alpha]_D$ — 52°) obtained from 4-bromofriedelin. The conversion of 4-bromofriedelin into alnusenyl acetate constitutes a partial synthesis of alnusenone from friedelin since alnusenyl acetate is readily converted into alnusenone by hydrolysis and oxidation.[3] The conversion of 4-bromofriedelin into alnusenone shows that friedelin and alnusenone have the same configuration at C_{10}. Furthermore, the formation of alnus-5(10)-en-3-one (XI) from 4-bromofriedelin by an ionic reaction

* Since the completion of our experiments Dr. David has kindly informed us that, starting from a pure sample of alnusenone, he has not been able to repeat the conversion into taraxerone. It would appear that the ketone used by Chapon and David,[2] and named "glutinone" by them, was not homogeneous.

[6] G. Brownlie, F. S. Spring, R. Stevenson and W. S. Strachan *J. Chem. Soc.* 2419 (1956).

[7] E. J. Corey and J. J. Ursprung *J. Amer. Chem. Soc.* **77**, 3667, 3668 (1955); **78**, 5041 (1956).

is strong support for the view that the 5-methyl group and the 10-hydrogen atom in friedelin are axially bonded.

The identification of alnusenone supports currently accepted views[8] on the biogenesis of the pentacyclic triterpenoids from a squalenoid precursor via a common ion (XVIII) or its equivalent. The degeneration of this ion may give rise to germanicol, olean-13(18)-enol, β-amyrin, taraxerol (taraxerone), *epi*alnusenol (whence alnusenone) and friedelin and, accordingly, alnusenone is represented as a stabilised intermediate in the biogenesis of friedelin.

EXPERIMENTAL*

Treatment of alnusenyl acetate with sodium amyloxide. Sodium (1·5 g) was added to a solution of alnusenyl acetate (500 mg) in amyl alcohol (60 cm^3) and the mixture refluxed for 17 hr. The product, isolated in the usual way, was heated with acetic anhydride and pyridine at 100° for 30 min. Crystallisation from chloroform–methanol gave alnusenyl acetate as needles (420 mg), m.p. and mixed m.p. 233–235°, $[\alpha]_D$ + 45°.

Treatment of alnusenyl acetate with monoperphthalic acid. A solution of alnusenyl acetate (250 mg) in chloroform (25 cm^3) at 0° was treated with a solution of monoperphthalic acid (1·2 mole) in ether and the mixture kept at 0° for 18 hr. The product, obtained in the usual way, crystallised from chloroform–methanol to give 5ξ : 6ξ-*epoxyalnusan-3*α*-yl acetate* (190 mg) as needles m.p. 225–227°, $[\alpha]_D \pm 0°$, +1·8° (Found: C, 79·4; H, 10·95; $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8 per cent). It does not give a colour with tetranitromethane in chloroform and it does not show selective absorption between 2000 and 3000 Å.

The epoxide was unchanged (m.p. and mixed m.p. 224–227°, $[\alpha]_D$ + 2°) after refluxing for 2 hr with excess lithium aluminium hydride in ether, followed by acetylation of the product, and it was also recovered unchanged (m.p. and mixed m.p. 224–227°, $[\alpha]_D$ 0°), after shaking its acetic acid solution with platinum and hydrogen for 5 hr.

Treatment of alnusenyl acetate with osmium tetroxide. Osmium tetroxide (350 mg) in ether (5 cm^3) was added to a solution of alnusenyl acetate (507 mg) in pyridine (50 cm^3) and the mixture kept in the dark for 21 days at room temperature. After dilution with ether, the mixture was refluxed for 1 hr with lithium aluminium hydride (750 mg). The product was isolated in the usual manner and treated with acetic anhydride and pyridine for 18 hr at room temperature. A solution of the dry acetylated product in light petroleum–benzene (9 : 1; 70 cm^3) was chromatographed on alumina (15 g). Light petroleum–benzene (9 : 1; 300 cm^3) eluted fractions which crystallised from chloroform–methanol to give alnusenyl acetate (85 mg) as needles, m.p. and mixed m.p. 232–235°, $[\alpha]_D$ + 43°. Light petroleum–benzene (1 : 1; 400 cm^3) and benzene (400 cm^3) eluted fractions which crystallised from chloroform–methanol to give 3α : 6ξ-*diacetoxyalnusan-5*ξ*-ol* (300 mg) as needles, m.p. 266–268°, $[\alpha]_D \pm 0°$ (Found: C, 75·1; H, 10·5. $C_{34}H_{56}O_5$ requires C, 74·95; H, 10·4 per cent). It does not show selective absorption between 2000 and 3000 Å. Infra-red absorption (in Nujol): Bands at 1730, 1230 (acetate), 3570, 1033 and 970 cm^{-1} (hydroxyl). It does not give a colour with tetranitromethane in chloroform.

The triol diacetate (85 mg) in acetic acid (50 cm^3) was treated at room temperature

* Specific rotations are for 1–2 per cent solutions in chloroform at 15 ± 5°. A light petroleum fraction, b.p. 60–80° and Grade II alumina were used for chromatography.

[8] A. Eschenmoser, L. Ruzicka, O. Jeger and D. Arigoni *Helv. Chim. Acta* **38**, 1890 (1955).

with chromium trioxide (1·2 mole) in acetic acid (10 cm³), added with stirring during 10 min, and the mixture kept at room temperature for 18 hr. The triol diacetate (60 mg) was recovered as needles from chloroform–methanol, m.p. and mixed m.p. 265–268°, $[\alpha]_D + 1°$.

Conversion of alnusene (V) *into olean*-13(18)-*ene* (VI) *and* 18α-*olean*-12-*ene* (VII). A solution of alnusene[3,4] (m.p. 181°, $[\alpha]_D + 56°$) (205 mg) in acetic acid (250 cm³) containing concentrated hydrochloric acid (60 cm³) was refluxed for 20 hr. Crystallisations of the product from chloroform–methanol gave the mixture of olean-13(18)-ene and 18α-olean-12-ene (100 mg) as blades m.p. 185–186°, $[\alpha]_D - 19°$, $- 18·5°$, undepressed in m.p. when mixed with a specimen (m.p. 186–187°, $[\alpha]_D - 18°$) prepared by the same acid treatment of olean-12-ene. The infra-red absorption spectra of the two specimens are identical.

Alnusa-1(10):5-*dien*-3α-*yl acetate* (IX, R = Ac). Selenium dioxide (1 g) in acetic acid (96 per cent, 26 cm³) was added to a solution of alnusenyl acetate (1 g) in glacial acetic acid (250 cm³), and the mixture kept at 60–70° for 1 hr. A solution of the product, obtained in the usual way, in light petroleum (60 cm³) was chromatographed on alumina (30 g). Light petroleum (600 cm³) eluted fractions which crystallised from chloroform–methanol to give alnusa-1(10):5-dien-3α-yl acetate (650 mg) as needles, m.p. 164–166°, $[\alpha]_D + 35°$; λ_{max} 2300 and 2380 Å (ε = 16,000 and 18,000), inflection at 2480 Å (ε = 11,000) (Found: C, 82·2, H, 11·0. Calc. for $C_{32}H_{50}O_2$: C, 82·3; H, 10·8 per cent). It gives a brown colour with tetranitromethane. Chapon[4] gives m.p. 163°, $[\alpha] + 33°$.

Alnusa-1(10):5-*dien*-3α-*ol* (IX, R = H). A solution of alnusadienyl acetate (250 mg) in ether (50 cm³) was refluxed with lithium alumium hydride (300 mg) for 20 min. Working up in the usual manner gave *alnusa*-1(10):5-*dien*-3α-*ol* (210 mg) which separates from chloroform–methanol as needles; m.p. 195–197°, $[\alpha]_D + 83°$, λ_{max} 2320 and 2390 Å (ε = 14,500 and 17,000), inflection at 2480 Å (ε = 11,000) (Found: C, 85·2; H, 11·7. $C_{30}H_{48}O$ requires C, 84·8; H, 11·4 per cent). It gives a brown colour with tetranitromethane in chloroform.

Catalytic reduction of alnusa-1(10):5-*dien*-3α-*yl acetate.* (a) Alnusadienyl acetate (205 mg) in a mixture of *cyclo*hexane (45 cm³) and aqueous acetic acid (33 per cent w/w 20 cm³) was shaken with hydrogen and platinum (from 200 mg PtO_2) for 6 hr. Crystallisation of the product from chloroform–methanol gave alnus-5-en-3α-yl acetate (120 mg) as needles, m.p. and mixed m.p. 232–235°, $[\alpha]_D + 46°$. (b) A solution of alnusadienyl acetate (208 mg) in glacial acetic acid (150 cm³) was shaken with hydrogen and platinum (from 200 mg PtO_2) for 2½ hr. The product crystallised from chloroform–methanol to give alnusanyl acetate (135 mg) as small plates, m.p. and mixed m.p. 261–263°, $[\alpha]_D + 10°$, $+ 11°$.

Enol acetate from alnusenone. Concentrated sulphuric acid (1 drop) was added to a solution of alnusenone (160 mg) in *iso*propenyl acetate (25 cm³) and the mixture refluxed in nitrogen for 7 hr, with occasional removal of the condenser. Sodium acetate was added and the solvent removed. A solution of the product, isolated by means of ether, in benzene–light-petroleum (1 : 1; 30 cm³) was chromatographed on alumina (5 g). Benzene–light-petroleum (1 : 1; 200 cm³) eluted fractions which crystallised from chloroform–methanol to give the *alnusa*-2:5-*dien*-3-*yl acetate* (IV) (110 mg) as plates, m.p. 254–257°, $[\alpha]_D + 41°$, $\varepsilon_{2060} = 5800$ (Found: C, 82·2; H, 10·8. $C_{32}H_{50}O_2$ requires C, 82·3; H, 10·8 per cent). It gives a yellow colour with

tetranitromethane in chloroform. The enol acetate was hydrolysed by refluxing its solution in 5 per cent methanolic potassium hydroxide for 1½ hr. Crystallisation of the product from chloroform–methanol gave alnusenone as plates, m.p. and mixed m.p. 243–245°, $[\alpha]_D$ + 33°.

Pyrolysis of alnusenyl benzoate. Alnusenyl benzoate (m.p. 234–235°, $[\alpha]_D$ + 16°; 500 mg) was heated at 290–300° for 3 hr in nitrogen. A solution of the product in light petroleum (30 cm³) was chromatographed on alumina (15 g). Light petroleum (400 cm³) eluted fractions which crystallised from chloroform–methanol to give *alnusa*-2:5-*diene* (110 mg) as blades, m.p. 182–184°, $[\alpha]_D$ + 53°, + 52°, ε_{2110} = 6,500 (Found: C, 88·1; H, 12·2. $C_{30}H_{48}$ requires C, 88·2; H, 11·8 per cent). It gives a yellow colour with tetranitromethane in chloroform.

Oxidation of alnusa-1(10):5-*dien*-3α-*ol.* Alnusadienol (180 mg) in pyridine (10 cm³) was added to a slurry of chromium trioxide–pyridine complex (from 1 g CrO_3 and 10 cm³ pyridine) and the mixture kept at room temperature for 17 hr. The product was isolated using ether, and its solution in light petroleum (30 cm³) chromatographed on alumina (10 g). Benzene–light-petroleum (1 : 2; 100 cm³) eluted a fraction, crystallisation of which from methanol gave *alnusa*-1:5(10)-*diene*-3:6-*dione* (X) (50 mg) as pale yellow blades, m.p. 253–255°, $[\alpha]_D$ + 62°, + 63°, λ_{max} 2180 and 3190 Å (ε = 11,000 and 8,300) (Found: C, 82·5; H, 10·1; O, 7·3. $C_{30}H_{44}O_2$ requires C, 82·5; H, 10·2; O, 7·3 per cent). Alnusadienedione was unchanged (m.p. and mixed m.p. 252–255°, $[\alpha]_D$ + 62°) after refluxing its solution in acetic acid with *o*-phenylenediamine and sodium acetate for 2 hr.

Alnus-5(10)-*en*-3-*one* (XI). A solution of alnusenone (m.p. 245–246°, $[\alpha]_D$ + 31°; 1·0 g) in hot glacial acetic acid (500 cm³) was treated with concentrated hydrochloric acid (12 cm³) and the mixture heated on the steam-bath for 18 hr. The mixture was evaporated to dryness under reduced pressure and the residue crystallised from chloroform–methanol to give *alnus*-5(10)-*en*-3-*one* (650 mg) as plates, m.p. 250–252°, $[\alpha]_D$ − 90° (Found: C, 85·1; H, 11·3. Calc. for $C_{30}H_{48}O$: C, 84·8; H, 11·4 per cent). Chapon[4] gives m.p. 248°, $[\alpha]_D$ − 84°, for "ketone-II" prepared from alnusenone by treatment with sulphuric–acetic acid mixture. Alnus-5(10)-en-3-one gives a yellow colour with tetranitromethane in chloroform and a pink colour in the Zimmermann test.

Alnus-5(10)-*en*-3ξ-*ol* (XVII, R = H). A suspension of alnus-5(10)-en-3-one (200 mg) in dry ether (50 cm³) was treated at room temperature with lithium aluminium hydride (100 mg). The product, isolated in the usual manner, was thrice crystallised from light petroleum (b.p. 60–80°) to give *alnus*-5(10)-*en*-3ξ-*ol* as needles, m.p. 241–242°, $[\alpha]_D$ − 42° (Found: C, 84·8; H, 12·5. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8 per cent). Chapon[4] gives m.p. 229–231°, $[\alpha]_D$ ± 0° for "alcohol-II".

Alnus-5(10)-*en*-3ξ-*yl acetate* (XVII, R = Ac). (a) Acetylation of alnus-5(10)-en-3ξ-ol using acetic anhydride and pyridine at 100° for 30 min yielded *alnus*-5(10)-*en*-3ξ-*yl acetate*, separating from chloroform–methanol as plates, m.p. 290–293°, $[\alpha]_D$ − 27° (Found: C, 82·0, H, 11·4. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2 per cent). Chapon[4] gives m.p. 276–278°, $[\alpha]_D$ − 15° for the acetate of "alcohol-II". (b) A refluxing solution of alnus-5(10)-en-3-one (100 mg) in benzene (10 cm³) and ethanol (50 cm³) was treated portionwise during 15 min with sodium (2 g) and the mixture poured into water. The product was isolated using ether and acetylated with acetic anhydride and pyridine at 100° for 15 min. The acetylated product crystallised from

chloroform–methanol to give alnus-5(10)-en-3ξ-yl acetate as plates, m.p. and mixed m.p. 290–292°, $[\alpha]_D$ — 28°.

A suspension of alnus-5(10)-en-3ξ-yl acetate (55 mg) in dry ether (25 cm^3) was treated with lithium aluminium hydride (50 mg) and the mixture refluxed for 5 min. The product crystallised from light petroleum to give alnus-5(10)-en-3ξ-ol as fine needles, m.p. 244–245° (no depression), $[\alpha]_D$ — 42·5° (Found: C, 84·35; H, 11·5 per cent).

Alnusa-1:5(10)-*dien*-3-*one* (XII). A solution of alnus-5(10)-en-3-one (250 mg) in glacial acetic acid (125 cm^3) at 30° was treated over 5 min with a solution of bromine (95 mg) in acetic acid (6 cm^3). Hydrogen bromide was evolved and the solution gradually developed a light brown colour. After 5 min potassium acetate (3 g) was added, the colour immediately changing to bright yellow. The mixture was heated on the steam bath for 2 hr and evaporated under reduced pressure. The product was isolated by means of ether and its solution in light petroleum was chromatographed on a column of alumina (15 g). Elution with light petroleum (400 cm^3) gave a fraction (38 mg) crystallisation of which from chloroform–methanol yielded unchanged alnus-5(10)-en-3-one, m.p. 240–244° (no depression). Elution of the column with light petroleum–benzene mixtures and with benzene yielded fractions (175 mg) of m.p.'s between 211–215° and 216–217°. These were combined and crystallised from chloroform–methanol to give *alnusa*-1:5(10)-*dien*-3-*one* (100 mg) as yellow plates, m.p. 216–217°, $[\alpha]_D$ — 30°, λ_{max} 2070 and 3220 Å (ε, 7000 and 5500) (Found: C, 85·4; H, 11·3. $C_{30}H_{46}O$ requires C, 85·2; H, 11·0 per cent). The yellow colour of a solution of the dienone in chloroform is intensified by the addition of tetranitromethane.

Enol acetate from alnusa-1:5(10)-*dien*-3-*one*. A solution of alnus a-1:5(10)-dien-3-one (50 mg) in *iso*propenyl acetate (20 cm^3) containing concentrated sulphuric acid (1 drop) was refluxed under nitrogen for 6 hr. After the addition of potassium acetate the solution was evaporated under reduced pressure and the product isolated by means of ether. Crystallisation from chloroform–methanol gave 3-*acetoxyalnusa*-2:1(10):5-*triene* (XIII) (30 mg) as pale yellow plates, m.p. 218–222°, $[\alpha]_D$ + 246°, λ_{max} 2040 and 3160 Å (ε, 7500 and 9100) (Found: C, 83·1; H, 10·7. $C_{32}H_{48}O_2$ requires C, 82·7; H, 10·4 per cent). A solution of the enol acetate in chloroform gives with tetranitromethane a brown colour which quickly fades.

Alnus-5(10)-*ene* (XIV). A mixture of alnus-5(10)-en-3-one (180 mg), hydrazine hydrate (100 per cent; 2 cm^3) and methanolic sodium methoxide (from 0·2 g sodium and 25 cm^3 methanol) was kept at 180° in an autoclave for 18 hr. The product, isolated in the usual way, crystallised from chloroform–methanol to give alnus-5(10)-ene (110 mg) as blades, m.p. 224–226°, $[\alpha]_D$ — 40°. Chapon[4] gives m.p. 225°, $[\alpha]_D$ — 38°.

Conversion of alnus-5(10)-*ene into olean*-13(18)-*ene and* 18α-*olean*-12-*ene*. A solution of alnus-5(10)-ene (110 mg) in acetic acid (125 cm^3) and concentrated hydrochloric acid (30 cm^3) was refluxed for 18 hr. Crystallisation of the product from chloroform–methanol gave the mixture (50 mg) of olean-13(18)-ene and 18α-olean-12-ene as blades, m.p. and mixed m.p. 185–186°, $[\alpha]_D$ — 19·5°.

Conversion of 4-*bromofriedelin* (XVI) *into alnusenone and alnus*-5(10)-*en*-3-*one*. 4-Bromofriedelin[2] (m.p. 198–199°, $[\alpha]_D$ + 88°; 375 mg) in ether (150 cm^3) was added to a solution of silver acetate (375 mg) in water (4 cm^3) and acetic acid (190 cm^3),

the mixture boiled until the vapour temperature was 110° and then refluxed for 20 min. The product crystallised from chloroform–methanol to give the mixed crystal of alnusenone and alnus-5(10)-en-3-one as plates (220 mg), m.p. 247–249°, $[\alpha]_D$ — 52°.

*Synthetic mixture of alnus-*5(10)*-en-*3*-one* (XI) *and alnusenone* (II). A mixture of alnus-5(10)-en-3-one (100 mg, m.p. 250–252°, $[\alpha]_D$ — 90°) alnusenone (50 mg, m.p. 245–246°,$[\alpha]_D$ + 31°) was crystallised from chloroform–methanol to give plates, m.p. 247–249°, $[\alpha]_D$ — 51°. Recrystallisation from the same solvent gave plates m.p. 247–249°, $[\alpha]_D$ — 51·5°, undepressed in m.p. when mixed with the specimen prepared from 4-bromofriedelin.

*Alnusenyl acetate and alnus-*5(10)*-enyl acetate from friedelin.* A solution of the mixture (220 mg) of alnusenone and alnus-5(10)-en-3-one (prepared from friedelin) in ether (30 cm^3) and benzene (25 cm^3) was refluxed with lithium aluminium hydride (220 mg) for 20 min, and the product treated with acetic anhydride and pyridine on the steam-bath for 1 hr. Crystallisation from chloroform-methanol gave alnus-5(10)-enyl acetate as plates (80 mg) m.p. and mixed m.p. 290–292°, $[\alpha]_D$ — 25°. Concentration of the mother liquors gave a mixture of plates and needles, which was washed on the filter with chloroform–methanol (1 : 1) until only plates remained. Concentration of the washings gave needles (50 mg) which crystallised from chloroform–methanol to give alnusenyl acetate as needles (30 mg), m.p. and mixed m.p. 233–236°, $[\alpha]_D$ + 44°. The infra-red absorption spectrum of this sample is identical with that of an authentic reference specimen of alnusenyl acetate.

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