221. *Miro Resin. Part I. Ferruginol.*

By C. W. BRANDT and L. G. NEUBAUER.

Ferruginol, a diterpenic resinol ($C_{20}H_{30}O$) isolated from the resin of *Podocarpus ferrugineus,* has been shown to be tricyclic and to possess three ethylenic linkages present in a phenolic nucleus. Catalytic hydrogenation gave the saturated hydrocarbon *ferruginane* ($C_{20}H_{36}$), which on selenium dehydrogenation afforded retene. Dehydrogenation of ferruginol yielded mainly a *retenol* together with lesser amounts of pimanthrene. The retenol is identical with one obtained by other workers from hinokiol, and described by them as a retene-carbinol. Evidence has now been brought forward to show that this retenol is phenolic, with the hydroxyl group residing at position 8. Provisional formulæ for ferruginol and ferruginane are suggested.

THE Miro tree (*Podocarpus ferrugineus*), endemic to New Zealand, slowly bleeds a soft sticky resin after incision of the bark. The resin, which was briefly examined by Easterfield (*Trans. N.Z. Inst.*, 1910, **43**, 53), has now been examined in some detail and the chemistry of its main constituent, a new diterpenic resinol, is described.

The crude resin, after removal of the steam-volatile oils and a proportion of resin acid, and fractional distillation under diminished pressure, yielded approximately 70% of a homogeneous, pale lemon, glassy resinol, b. p. 175°/0·3 mm., $[\alpha]_D^{16°} + 40·6°$, for which the name *ferruginol* is proposed. Analyses and molecular-weight determinations of the resinol and of several well-defined crystalline derivatives showed that the resinol has the formula $C_{20}H_{30}O$ and contains one hydroxyl group. It formed a *formate,* an *acetate,* a *benzoate,* and a non-crystalline *methyl* ether.

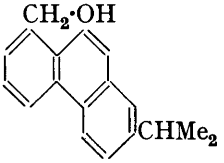
On treatment with phthalic anhydride at temperatures up to 230° ferruginol failed to yield an acid phthalate. Attempts to split out the hydroxyl group with phosphoric oxide, potassium bisulphate, formic acid or dilute sulphuric acid were unsuccessful. The slight but distinct solubility of ferruginol in aqueous sodium hydroxide suggested the presence of a phenolic group, also indicated by the formation of deep red and green colorations with diazotised sulphanilic acid and ferric chloride respectively. The xanthoproteic reaction indicated the presence of a benzenoid ring.

The unsaturated nature of ferruginol was also shown by the production of an intense brownish-yellow coloration with tetranitromethane in chloroform solution and by the rapid absorption of bromine in carbon tetrachloride solution. Neutral permanganate in acetone solution was slowly decolorised. Treatment in ethereal solution with dry hydrogen chloride or bromine at low temperatures failed to yield crystalline derivatives of ferruginol. The resinol, its methyl ether, and the supercooled acetate were sufficiently fluid at 60° to permit the determination of the refractive indices and densities by the usual methods; in all cases the molecular refractivities indicated that the resinol possesses three ethylenic linkages. Quantitative determinations of unsaturation with perbenzoic acid (Hibburt and Burt, *J. Amer. Chem. Soc.*, 1935, **47**, 2240) consistently agreed with the presence of three unsaturated linkages; iodine values indicated two, and bromine values (Reindel and Niederländer, *Annalen*, 1929, **475**, 147) two, three, and four such linkages according to the conditions of the reaction. The resinol was rather resistant to catalytic hydrogenation; hydrogen equivalent to no more than one ethylenic linkage was absorbed when the resinol was shaken in ethyl acetate solution with hydrogen in the presence of Adams's platinum oxide catalyst or palladium-charcoal of proven activity. The product was not homogeneous, since a considerable proportion of ferruginyl acetate was obtained upon acetylation. When hydrogenated in acetic acid solution, ferruginol slowly took up four molecules of hydrogen in the presence of Adams's catalyst. The hydrogenation was accompanied by elimination of the hydroxyl group and the formation of a saturated liquid hydrocarbon, *ferruginane*, $C_{20}H_{36}$. The same hydrocarbon was obtained with similar difficulty when ferruginyl acetate was hydrogenated in acetic acid solution. No condensation product could be isolated when ferruginol was heated with maleic anhydride, and reduction could not be effected with sodium in either ethyl or amyl alcohol. It is concluded that ferruginol possesses three ethylenic linkages, present in a phenolic group. The ferruginol molecule is thus tricyclic. The absorption spectrum of ferruginyl acetate in *cyclo*hexane shows a maximum at 2775 A., a fact which is consistent with the presence of a benzenoid ring. It is of interest that the unsaturated linkages in the phenolic group of œstrone can be reduced catalytically only in acidic solvents, and that the absorption curve recorded for ferruginol is very similar in form to that of œstrone in the same wave-length region.

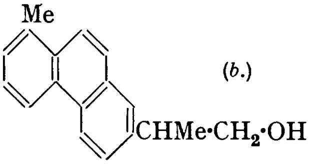
Dehydrogenation of ferruginol with selenium for 28—30 hours at various temperatures gave high yields of crystalline phenanthrene derivatives. When the reaction was conducted mainly at 320—340°, the product consisted of approximately 30% of pimanthrene and 70% of a *phenol*, $C_{18}H_{18}O$, m. p. 178°. When the temperature was maintained at 275—285° during the initial 24 hours and at 320—340° for a final four hours, the phenol only was obtained. Samples of ferruginane, obtained by hydrogenation of both the resinol and its acetate, were dehydrogenated with selenium at 280—345° for 27 hours. Both experiments furnished retene in approximately 70% yields.

The phenol $C_{18}H_{18}O$ formed a *picrate*, m. p. 176—177°, a *styphnate*, m. p. 172°, and an *acetate*, m. p. 90—91°. The last furnished an *acetoxy-quinone*, m. p. 188—189°, which on hydrolysis gave a *quinone*, m. p. 285° (decomp.). Treatment of the phenol with methyl sulphate failed to yield a methyl ether. When distilled in hydrogen over hot zinc dust, the phenol yielded 1-methylphenanthrene and pimanthrene, but under no conditions was retene or any other hydrocarbon of formula $C_{18}H_{18}$, which would be expected to result from the dehydroxylation of the phenol, obtained.

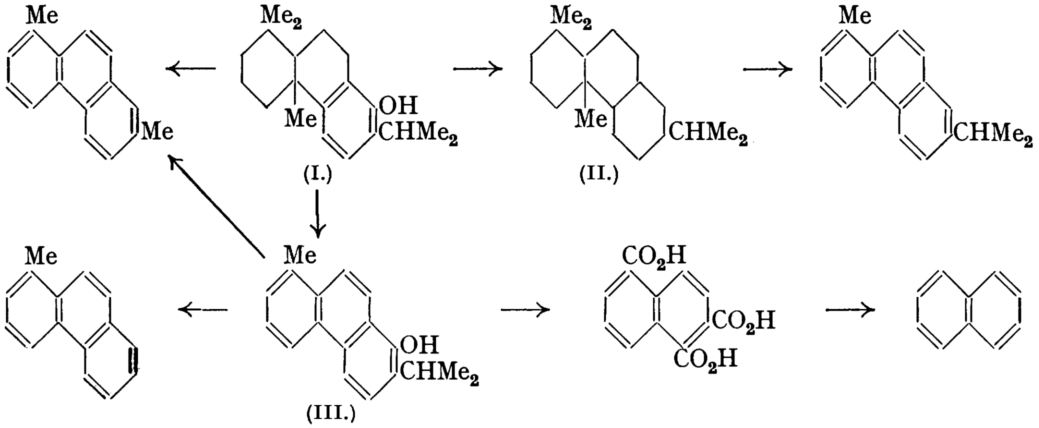
(*a*.)



(*b*.)



Four different hydroxyretenes have been recorded previously; of these, the melting points of 2- and 6-retenol and their derivatives (Komppa and Wahlforss, *J. Amer. Chem. Soc.*, 1930, **52**, 5009; Fieser and Young, *ibid.*, 1931, **53**, 4120) show them to be different from the product obtained from ferruginol. Identity with 9-retenol, m. p. 176° (Fieser and Young, *loc. cit.*), or the unrecorded 10-retenol is precluded because the unknown phenol yields a hydroxy-quinone. The fourth hydroxyretene, m. p. 176—177° (picrate, m. p. 176—177°; acetate, m. p. 94°; quinone, m. p. 190—191°; methyl ether, m. p. 82°), is one obtained by Keimatsu and Ishiguro by the dehydrogenation of hinokiol, a resinol from *Chamoecyparis obtusa* (*J. Pharm. Soc. Japan*, 1935, **55**, 186). These workers proposed the alternative structures (*a*) and (*b*) for this substance. Professor Keimatsu has kindly supplied us with a sample of the product from hinokiol. It possessed phenolic properties



similar to those of our product and mixed melting-point determinations of the two phenols and of their picrates (similar melting points, respectively) showed no depressions. It is concluded that the substances are identical and that the derivative described as a quinone in the Japanese publication was actually an acetoxy-quinone.

The hydroxyl group cannot be in position 1 or 7, since it has been shown that these are already substituted by the formation of pimanthrene on zinc dust distillation; positions 2, 6, 9, and 10 have already been excluded. The quinone gave a red ester with boracetic anhydride (Dimroth, *Ber.*, 1921, **54**, 3020; *Annalen*, 1926, **445**, 97, 123), which would fix the hydroxyl group at position 8, since according to this test hydroxy-quinones yield coloured boracetic esters only when the hydroxyl group is ortho to one of the carbonyl groups. The quinone failed to give the reversible colour reaction of Fieser and Young (*loc. cit.*, p. 4126) and thus positions 2, 4, 5, and 7 are excluded according to this test also; doubt, however, has been raised as to the general applicability of this reaction (Short and Stromberg, J., 1937, 516).

Further evidence in respect to the position of the hydroxyl group was sought by the oxidation of the retenol with potassium ferricyanide. It was expected that a structure similar to (*a*) or (*b*) would result in the formation of phenanthrene-1 : 7-dicarboxylic acid, but that a structure such as (III) might yield a hydroxy-acid or undergo ring fission. Keimatsu and co-workers have reported the oxidation of this phenol to phenanthrene-1 : 7-dicarboxylic acid (*J. Pharm. Soc. Japan*, 1936, **56**, 588), but we were unable to confirm this result. The oxidation provided naphthalene-1 : 5 : 6-tricarboxylic acid in good yield and the hydroxyl group has therefore been placed provisionally at position 8.

It is suggested that the formation of pimanthrene in addition to the retenol on the dehydrogenation of ferruginol is due to removal of the hydroxyl group together with a portion of the adjacent *iso*propyl side chain. Such a reaction would be in agreement with the presence of an aromatic system in ring III of the ferruginol molecule, for in that case no nuclear hydrogen would be available for removal with the hydroxyl group during dehydrogenation. It is also probable that the influence of the hydroxyl group on the *iso*propyl side chain is again apparent in the zinc dust degradation of the retenol, where the formation of pimanthrene and 1-methylphenanthrene represents successive stages in the splitting out of this side chain.

It is concluded that eighteen of the carbon atoms in both ferruginol (I) and ferruginane (II) are arranged as in retene. The two remaining carbon atoms have been provisionally placed as quaternary methyl groups by analogy with the general structure of diterpenic compounds related to phenanthrene.

EXPERIMENTAL.

Ferruginol.—The crude material (500 g. of a dark brown semi-solid resin) was collected during several months by bleeding from V-shaped grooves cut in the bark of a number of Miro trees. On steam distillation the resin yielded 20% of volatile oil, which on fractional distillation gave 90% of α-pinene, $[\alpha]_D^{16^\circ}$ + 10·4°, identified by the mixed m. p.'s of the nitrosochloride and the nitrolpiperide and the preparation of camphene by treatment with dry hydrogen chloride. The remaining 10% of the oil consisted of a terpene having physical constants similar to those of β-pinene. The residual solid resin (395 g.) was dissolved in ether and filtered to remove wood particles and other foreign matter. Extraction of the ethereal solution with aqueous ammonium carbonate and sodium carbonate yielded only traces of acidic material, but a blue amorphous solid appeared at the junction of the liquids and was removed by filtration (5 g.); it was not further examined. Extraction with 4% sodium hydroxide solution yielded a resin acid (19 g.), an account of which will appear in a later paper. The ethereal solution, after washing and drying, yielded a brown vitreous resin (366 g.), which, when distilled in six portions at 0·4 mm. pressure, gave the following fractions (all distillations from oil or metal baths): (1) 110—175°, 23·4 g. of a pale yellow oil; (2) 175—180°, 90·6 g. of a pale semi-solid resin; (3) 180—184°, 126·6 g. of a pale vitreous resin; (4) 185—200°, 89·4 g. of a light brown resin; residue, 33·0 g. of a dark brown resin. Systematic redistillation of fractions (2), (3), and (4) gave 212 g. of a pale amber-coloured vitreous resin. This substance, *ferruginol*, distilled constantly at 175°/0·3 mm. and had $[\alpha]_D^{16^\circ}$ + 40·6° (in 14% ethyl-alcoholic solution); $d_{4^\circ}^{61^\circ}$ 1·008, $n_D^{61^\circ}$ 1·5346, hence $[R_L]_D = 88{\cdot}4$ (calc. for $C_{20}H_{30}O|_{\overset{=}{3}}$, 88·1) [Found: C, 83·4, 83·8, 83·5;

H, 10·6, 10·7, 10·6; *M* (cryoscopic in benzene), 282. $C_{20}H_{30}O$ requires C, 83·8; H, 10·6%; *M*, 286]. With perbenzoic acid, ferruginol absorbed oxygen equivalent to 3·1 and 3·2 ethylenic linkages. Iodine values indicated 1·7, 1·8, 2·3, and 2·3 such linkages according to the conditions of the determination.

Tests for phenolic properties. (1) Ferruginol (0·2 g.) in xylene (10 c.c.) was shaken successively with 10 c.c. portions of sodium hydroxide solutions varying in concentration from 0·5 to 15%. The filtered extracts, when acidified, all gave white, more or less flocculent, precipitates varying from a slight opalescence in the case of the 0·5% extract to a moderately large rapidly flocculating precipitate from the 15% extract. These precipitates were insoluble in sodium carbonate solution, but dissolved readily in excess of sodium hydroxide solution. (2) Ferruginol gave a permanent brownish-green coloration with alcoholic ferric chloride. (3) The resinol in aqueous-alcoholic sodium hydroxide solution gave a deep red coloration on addition of diazotised sulphanilic acid.

Xanthoproteic reaction. Ferruginol or its acetate, when treated with warm concentrated nitric acid, became yellow and partly dissolved; dilution with water then produced yellow precipitates. The solutions and the precipitates changed to a deep orange colour when neutralised with ammonia.

Ferruginyl formate. Ferruginol (5·4 g.) was refluxed for 2½ hours with excess of formic acid containing two drops of sulphuric acid; the mixture was poured into water and neutralised with sodium carbonate. Ether extracted a resinous product (5·5 g.), which was shown by saponification to contain 45% of the ester. The crude ester was distilled at 0·3 mm.: (1) 170°, 1·3 g.; (2) 170°, 1·3 g.; (3) 170—175°, 1·0 g. All the fractions were crystalline. The *formate*, crystallised from methyl alcohol and finally from light petroleum, formed white needles, m. p. 96—97° (Found: C, 79·8, 80·1; H, 9·7, 9·7; saponification equiv., 310. $C_{21}H_{30}O_2$ requires C, 80·2; H, 9·6%; saponification equiv., 314).

Ferruginyl acetate. A mixture of ferruginol (3 g.), acetic anhydride (10 c.c.), and fused sodium acetate (1·75 g.) was refluxed for 1½ hours. After cooling, the mixture was poured into water, heated on the water-bath, and extracted with ether. The extract, after washing and drying, yielded a viscous yellow product (3·2 g.), which soon crystallised. The *acetate*, after distillation (b. p. 165°/0·4 mm.) and crystallisation from methyl alcohol and finally from light petroleum, formed white needles, m. p. 81—82° [Found: C, 80·4, 80·5, 80·5, 80·3; H, 9·8, 9·9, 9·9, 9·8; saponification equiv., 333; *M* (cryoscopic in benzene), 323. $C_{22}H_{32}O_2$ requires C, 80·4; H, 9·8%; *M*, 328]. $[\alpha]_D^{16°} + 60·3°$ (10% solution in alcohol); $d_{4°}^{61°}$ 1·013, $n_D^{61°}$ 1·5186 (determined on the super-cooled ester); hence $[R_L]_D = 98·3$ (calc. for $C_{22}H_{32}O_2|\overset{=}{3}$, 97·3).

The curve for a part of the absorption spectrum of ferruginyl acetate in *cyclo*hexane solution is shown in Fig. 1. Examinations of absorption spectra recorded in this paper were carried out by Mr. S. H. Wilson, Dominion Laboratory, New Zealand.

Ferruginyl benzoate. Ferruginol (5·9 g.) in pyridine (25 c.c.) was cooled in ice, and benzoyl chloride (3·5 c.c.) slowly added with shaking. After standing at room temperature for 12 hours, the mixture was heated on the water-bath (2 hours), washed until it was neutral, and extracted with ether. The oily crystalline product (7·4 g.) was crystallised from light petroleum (yield, 6·0 g.; *ca.* 75%). Further recrystallisation gave white needles, m. p. 154—155° (Found: C, 82·8, 83·3; H, 8·8, 8·9; saponification equiv., 394. $C_{27}H_{34}O_2$ requires C, 83·1; H, 8·8%; saponification equiv., 391). When the Schotten–Baumann method was used, a yield of approximately 50% of the *benzoate* was obtained.

Ferruginyl methyl ether. When ferruginol, either suspended in 2N-sodium hydroxide or dissolved in 90% alcohol, was treated with methyl sulphate, the products obtained had methoxyl contents equivalent to 18% and 50% respectively of *ferruginyl methyl ether.* An almost theoretical yield was obtained when ferruginol (4·7 g.) was ground with anhydrous potassium carbonate (3·4 g.) and refluxed (4 hours) in xylene with methyl sulphate (3 c.c., added in small portions) (Haworth and Lapworth, J., 1930, 2166). The liquid was filtered and washed, and the xylene removed under diminished pressure. The residual soft amber-coloured resin (4·9 g.) contained 10·3% of methoxyl. It could not be crystallised and was distilled at 0·3 mm.: (1) 163—166°, 2·1 g.; (2) 166°, 1·9 g.; (3) 166—167°, 0·3 g. Fractions (1) and (2) were pale-coloured semi-solid resins. Fraction (2) had $d_{4°}^{61°}$ 0·9868, $n_D^{61°}$ 1·5290; hence $[R_L]_D = 93·9$ (calc. for $C_{21}H_{34}O|\overset{=}{3}$, 92·9) (Found: C, 83·4, 83·3; H, 10·4, 10·4; OMe, 10·3. $C_{21}H_{32}O$ requires C, 83·9; H, 10·7; OMe, 10·3%).

Catalytic Hydrogenation.—(i) *Ferruginol in ethyl acetate.* When hydrogenated in ethyl acetate solution in the presence of Adams's platinum oxide catalyst, ferruginol (1·3 g.) absorbed hydrogen equivalent to one ethylenic linkage (4 hours). No further reduction could be effected after distillation of the semi-solid resinous product. Experiments in the same solvent at 60°, with hydrogen at 3 atms., gave similar results. When 10% palladium–charcoal catalyst was used under the same conditions, only ½ molecule of hydrogen was absorbed. Although analyses and the molecular refraction of the apparent dihydro-product were in agreement with the formula $C_{20}H_{32}O|_{\overline{2}}$, the product was not homogeneous, since acetylation provided a 40% yield of ferruginyl acetate.

(ii) *Ferruginol in acetic acid.* Ferruginol (8 g.) and Adams's catalyst (0·12 g.) in acetic acid (90 c.c.) were shaken with hydrogen at 3 atms.; 500 c.c. were absorbed during 8 hours and after reactivation with oxygen and several additions of fresh catalyst a further 75 c.c. were slowly absorbed. The solution was filtered and poured into water. After neutralisation with sodium carbonate and extraction with ether, a pale amber, semi-solid, still highly unsaturated resin (7·8 g.) was obtained. This was distilled under diminished pressure and again reduced in acetic acid solution. After these processes of reduction and distillation had been repeated six times, approximately 2500 c.c. of hydrogen had been absorbed during 61 hours. The product was a colourless limpid oil (3 g.) which was saturated to bromine in carbon tetrachloride and gave only a very faint coloration with tetranitromethane in chloroform. Fractional distillation of the oil gave *ferruginane* (1·2 g.), b. p. 139—140°/0·3 mm., $[\alpha]_D^{18^\circ}$ + 34·7° (5% solution in ethyl alcohol) (Found : C, 87·0, 86·9, 86·8; H, 13·1, 13·0, 13·2. $C_{20}H_{36}$ requires C, 86·9; H, 13·1%); $d_{4^\circ}^{25^\circ}$ 0·9350, $n_D^{25^\circ}$ 1·5077, hence $[R_L]_D = 88·1$ (calc. for $C_{20}H_{36}|_{\overline{0}}$, 88·0).

FIG. 1.
Ferruginyl acetate in cyclo*hexane.*

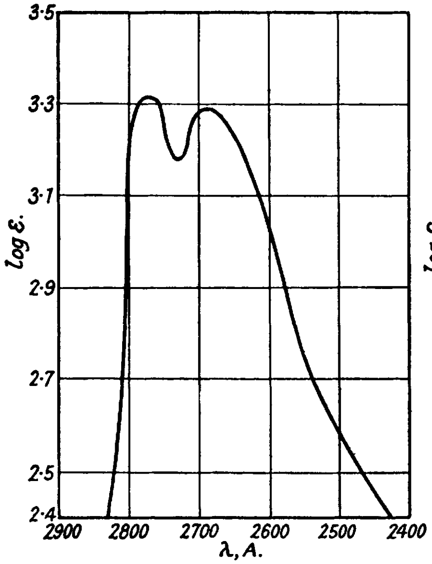
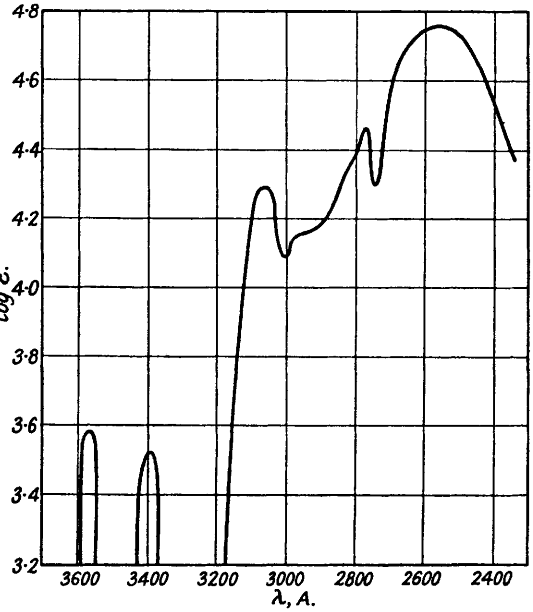


FIG. 2.
Retenol in cyclo*hexane.*



Dehydrogenation of Ferruginol with Selenium.—(i) Ferruginol (24 g.) was heated with selenium (24 g.) at 280—320° for 2 hours, at 320—340° for 27 hours, and at 350° for 1 hour. Extraction of the cooled mixture with ether yielded a light brown, crystalline mass (21·4 g.), which was distilled at 0·4 mm. : (1) 140—162°, 0·9 g. of a light brown oil containing traces of crystals, (2) 163—174°, 2·3 g. of light brown crystals, (3) 175—205°, 15 g. of crystals. Fraction (2) was recrystallised from alcohol, giving white platelets, m. p. 85—86°, of pimanthrene (Found : C, 93·3, 93·1; H, 6·9, 6·8. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). Its picrate, m. p. 130° (Found : C, 60·5; H, 4·0. Calc. : C, 60·7; H, 3·9%), and styphnate, m. p. 159°, both formed yellow needles from alcohol, and all three substances showed no depression in m. p. in admixture with authentic specimens. Fraction (3) was recrystallised from alcohol and finally from benzene, giving white needles, m. p. 178—179° (Found : C, 86·3, 86·5, 86·5, 86·1; H, 7·2, 7·3, 7·4, 7·3. $C_{18}H_{18}O$ requires C, 86·4; H, 7·2%). This *retenol* was moderately readily soluble in caustic alkali solution but insoluble in alkali carbonate solution; it gave a permanent green coloration with alcoholic ferric chloride, and a deep red coloration with diazotised sulphanilic acid in aqueous-alcoholic sodium hydroxide.

A portion of the absorption spectrum of the retenol in *cyclo*hexane solution is shown in Fig. 2.

(ii) Ferruginol (19 g.) was heated with selenium (20 g.) at 275—285° for 24 hours, then at 320—330° for 2 hours, and finally at 330—340° for 2 hours. Extraction of the reaction mixture with ether gave a crystalline product (18 g.), which was distilled at 0·3 mm.: (1) 133—150°, 3·1 g.; (2) 150—160°, 1·7 g.; (3) 165—195°, 12·9 g. Fractions (1) and (2) were oils containing small quantities of the retenol; they failed to yield a picrate or styphnate and were not further examined. Fraction (3) consisted of the retenol. No other aromatic product could be isolated.

Dehydrogenation of Ferruginane with Selenium.—Ferruginane (1·1 g., prepared by catalytic hydrogenation of ferruginol) was heated with selenium (2 g.) for 27 hours at 280—345°. Extraction of the cold reaction mixture with ether gave a crystalline product (0·9 g.), which was distilled from sodium at 0·3 mm.: (1) 145—160°, 0·15 g. of oily crystals, (2) 160—170°, 0·65 g. of white crystals. Fraction (2) after recrystallisation from alcohol gave white platelets (0·3 g.), m. p. 98°, not depressed by retene (Found: C, 92·3; H, 7·7. Calc. for $C_{18}H_{18}$: C, 92·3; H, 7·7%). The picrate, m. p. 125—126° (Found: C, 62·1; H, 4·7. Calc.: C, 62·2; H, 4·6%), and the styphnate, m. p. 140°, both formed yellow needles from alcohol and their m. p.'s were not depressed by authentic specimens. Fraction (1), when recrystallised, provided a further small quantity of retene.

Investigation of the Retenol $C_{18}H_{18}O$.—(i) *Derivatives.* The *picrate* crystallised in brick-red needles, m. p. 176—177° [Found: C, 60·1; H, 4·5; *M* (titration with 0·0119N-barium hydroxide), 488, 486. $C_{18}H_{18}O,C_6H_3O_7N_3$ requires C, 60·1; H, 4·4%; *M*, 480], and the *styphnate* in pale orange-red needles, m. p. 172° (Found: C, 58·2; H, 4·3. $C_{18}H_{18}O,C_6H_3O_8N_3$ requires C, 58·2; H, 4·3%), both from alcohol. The *acetate*, prepared by refluxing the retenol (2 g.) for 1 hour with acetic anhydride (12 c.c.) and fused sodium acetate (5 g.), crystallised from alcohol in white needles, m. p. 90—91° (Found: C, 82·0, 82·1; H, 7·0, 7·0. $C_{20}H_{20}O_2$ requires C, 82·1; H, 6·9%). The acetate (1 g.) in glacial acetic acid (3 c.c.) was heated on the water-bath (2 hours) with a solution of chromic acid (1·6 g.) in acetic acid (10 c.c.) and water (2 c.c.). The crystals which separated overnight were washed with 65% alcohol and recrystallised from methyl alcohol, giving orange-yellow needles, m. p. 188—189°, of the *acetoxy-quinone* (Found: C, 74·3; H, 5·7. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%). When this (0·3 g.) was refluxed for 1 hour with 0·5N-alcoholic potassium hydroxide (10 c.c.) and the crystals which separated after acidification were recrystallised from a large volume of alcohol (sparingly soluble in the common solvents), minute brick-red needles, m. p. 284—285°, of the *quinone* were obtained (Found: C, 76·7; H, 5·8. $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·8%).

(ii) *Dehydroxylation.* The retenol (4 g.) was intimately mixed with fine zinc dust (50 g.) and slowly distilled in a stream of hydrogen over a 30 cm. layer of red hot pumice–zinc dust in a combustion tube. The condensate of yellow oily crystals (2·1 g.) was distilled at 0·3 mm.: (1) 150—160°, 0·8 g.; (2) 160—170°, 0·7 g.; (3) above 170°, 0·3 g. All the fractions were pale yellow or white crystals. Fraction (1) was recrystallised from ethyl alcohol and yielded finally a substance (0·1 g.), m. p. 119—120°. Fraction (2) (m. p. 95—100°) after five recrystallisations gave 0·1 g. of unchanged retenol. Fraction (3) consisted almost entirely of unchanged retenol. All the mother-liquor residues from fraction (1) and the first two from fraction (2) were combined (1·0 g. of oily crystals) and distilled from sodium at 0·3 mm.: (1*a*) 140—145°, 0·6 g.; (2*a*) 145—160°, 0·2 g. Fraction (1*a*), when recrystallised from alcohol and finally from light petroleum, yielded a further quantity (0·12 g.) of the substance, m. p. 119—120° (Found: C, 93·7; H, 6·4. Calc. for $C_{15}H_{12}$: C, 93·7; H, 6·3%); this m. p. and that of the picrate (yellow needles from alcohol, m. p. 134—135°) were not depressed by authentic specimens of 1-methylphenanthrene (m. p. 119—120°), and its picrate (m. p. 134—135°) respectively. The residues from the early mother-liquors of fraction (1*a*) were combined; recrystallisation yielded white platelets of pimanthrene (0·14 g.), m. p. 85—86°, which formed a picrate, m. p. 130°, and a styphnate, m. p. 158—159°, both crystallising from alcohol in yellow needles. The m. p.'s of all three substances were unaltered in mixtures with authentic specimens. Recrystallisation of fraction (2*a*) yielded a further small quantity of pimanthrene. The first mother-liquor from fraction (3) yielded a substance (white platelets), m. p. 225°, which formed a picrate (brown needles), m. p. 173°, but the amount was too small for complete purification.

(iii) *Oxidation.* The retenyl acetate (1·8 g.) was stirred at 85—90° with a solution of potassium ferricyanide (288 g.) and potassium hydroxide (21 g.) in water (400 c.c.) for 90 hours, further amounts of potassium ferricyanide (115 g. and 50 g.) and of potassium hydroxide (21 g. and 10 g.) being added after 30 and 60 hours. The solution was cooled and filtered; the residual salt mass was pressed out on the filter and extracted with ether, whereby 0·4 g. of the retenol was obtained. The aqueous filtrate was acidified and extracted continuously with ether for 4 hours. The ethereal solution was washed twice with small quantities of water and then dried; removal of the ether yielded an acid (1·2 g.) in minute white crystals, m. p. 262—265°, slightly soluble in ether, moderately readily soluble in water, and easily soluble in methyl alcohol; after recrystallisation from methyl alcohol and washing with ether the m. p. was 270° [Found: C, 60·1; H, 3·5; (micro), *M* (titration with N/10-sodium hydroxide) for a tricarboxylic acid, 257. Calc. for $C_{13}H_8O_6$: C, 60·0; H, 3·1%; *M*, 260]. The acid (0·2 g.) was heated with calcium oxide and soda-lime, decomposition being complete at 380—400° after 20 minutes. The pale yellow, crystalline distillate (0·06 g.) had a naphthalene-like odour and after recrystallisation from alcohol formed white shining platelets, m. p. 80°, unaltered on admixture with naphthalene. The m. p. 147° of the picrate (lemon-yellow needles from acetic acid and finally from alcohol) was not depressed by naphthalene picrate (m. p. 148°).

Preparation of Naphthalene-1 : 5 : 6-*tricarboxylic Acid.*—1 : 5 : 6-Trimethylnaphthalene was prepared by the dehydrogenation, with selenium, of 5 g. of manoyl oxide (Hosking and Brandt, *Ber.*, 1935, **68**, 37). After regeneration from the pure picrate and distillation in a high vacuum (b. p. 115°/0·3 mm.) the hydrocarbon (0·5 g.) was oxidised with potassium ferricyanide in a manner similar to that described by Heilbron and Wilkinson (J., 1930, 2546). The resulting acid (0·4 g.), after being crystallised from methyl alcohol and washed with ether, formed minute white crystals, m. p. 270°, not depressed by the acid obtained by oxidation of the retenol. which it resembled in solubility.

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DOMINION LABORATORY, WELLINGTON, NEW ZEALAND.

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