116. *Totarol. Part I.*

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The dextrorotatory diterpene alcohol, totarol, m. p. 127°, was first isolated by Easterfield and McDowell (*Trans. New Zealand Inst.*, 1911, **43**, 55; 1915, **48**, 518) from the wood of the totara tree (*Podocarpus totara*). We have been encouraged by Professor Easterfield to continue the work which he initiated and the present communication describes an investigation on the structure of totarol. Easterfield proposed the formula $C_{20}H_{30}O$, and concluded that the compound is an alcohol, since it was neutral and afforded a crystalline acetate. The compound was believed to be a tertiary alcohol, since it was acetylated slowly.

Although the melting point of totarol has been raised to 132°, the analytical figures still agree with the formula $C_{20}H_{30}O$ and this is fully confirmed by an examination of the derivatives of totarol. The alcohol was converted into a *formate*, $C_{21}H_{30}O_2$, m. p. 125·5°, by boiling with concentrated formic acid, and remained unchanged when heated with phosphoric oxide in xylene solution or with phthalic anhydride in benzene solution. Phthalic anhydride at 140°, however, converted totarol into a *hydrogen phthalate*, m. p. 161—163°, and it may therefore be concluded that the alcoholic group is secondary.*

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* Oxidation experiments will be reported in a subsequent communication.

Totarol is unsaturated, since it gives a red colour with tetranitromethane and absorbs bromine very rapidly. The molecular refraction was determined in quinoline and acetophenone solution, since Krollpfeiffer (*Annalen*, 1923, **430**, 161) has shown that these solvents have the smallest influence on the molecular refraction of a dissolved substance and they have already been successfully applied in the resin acid series (Sherwood and Short, *Rep. Austral. Assocn. Sci.*, 1933, **31**, 33). The results agreed with the conclusion that totarol is tricyclic and contains three ethylenic linkages. A quantitative study of the action of perbenzoic acid upon totarol and *totaryl methyl ether*, m. p. 92—92·5°, prepared by the action of methyl iodide upon potassium totaryl oxide, also showed the presence of three unsaturated linkages.

Totarol is resistant to catalytic reduction, and hydrogenation was effected in acetic acid solution at 70° in presence of palladium–charcoal with hydrogen at a pressure of 30 lb. per sq. in. The product consisted of a saturated lævorotatory *hydrocarbon* (*totarane*), $C_{20}H_{36}$, m. p. 74·5—75°, and a smaller quantity of *dihydrototarol*, $C_{20}H_{32}O$, m. p. 151°. The dihydro-compound was slowly reduced by the catalytic method to *tetrahydrototarol*, $C_{20}H_{34}O$, m. p. 134·5°, but attempts to obtain the saturated alcohol $C_{20}H_{36}O$ have so far been unsuccessful. It is improbable that the ethylenic linkages in totarol are conjugated, since the alcohol does not react with maleic anhydride, neither is it reduced by sodium in ethyl- or amyl-alcoholic solution.

Dehydrogenation of totarol with selenium at 320° afforded a 70% yield of a *phenol*, $C_{15}H_{12}O$, m. p. 191°, which furnished a *methyl ether*, m. p. 133°, and an *acetate*, m. p. 136°. The methyl ether united with picric acid to form an unstable picrate and it was concluded that the phenol $C_{15}H_{12}O$ is a hydroxymethylphenanthrene; this conclusion was confirmed by the preparation of an orange-yellow *quinone*, $C_{17}H_{12}O_4$ (*quinoxaline*, m. p. 244·5—246·5°), by the oxidation of the acetate. When the phenol was distilled with zinc dust, 1-methylphenanthrene was obtained, so this compound must be a 1-methylphenanthrol. The hydroxyl group cannot reside at position 9 or 10, and positions 2, 4, 5 and 7 were apparently excluded by the observation that the corresponding 9 : 10-quinone did not give the reversible colour reaction stated by Fieser and Young (*J. Amer. Chem. Soc.*, 1931, **53**, 4126) to be characteristic of hydroxyphenanthra-9 : 10-quinones containing a hydroxyl group in the *m*-position to either of the carbonyl groups. Position 8 was excluded, since the hydroxy-quinone did not yield a coloured ester with boroacetic anhydride (Dimroth, *Ber.*, 1921, **54**, 3020; *Annalen*, 1926, **445**, 97, 123). Syntheses of 3- and 6-hydroxy-1-methylphenanthrene were effected (this vol., p. 510, and forthcoming publication), but neither was identical with the compound obtained from totarol. Of the remaining positions, 7 appeared to be the most probable on phyto-chemical grounds and a synthesis of 7-hydroxy-1-methylphenanthrene (J., 1936, 319) showed that this substance is identical with the phenol obtained from totarol. It is therefore clear that Fieser's colour reaction is not invariably diagnostic. 7-Hydroxy-1-methylphenanthrene is also produced by the dehydrogenation of totarol with sulphur or with palladium–charcoal.

An attempt was made to determine the way in which five carbon atoms of totarol are eliminated by an analysis of the gases produced during the catalytic dehydrogenation, but was rendered abortive by resinification and inconstancy in composition. The gas evolved was therefore partly condensed in liquid air and the temperature of the liquid was then allowed to rise slowly. The liquid phase persisted almost up to the boiling point of propane (— 46·5°), so totarol probably contains an *iso*propyl group, which is eliminated during dehydrogenation. In this connection, the dehydrogenation of totarane afforded interesting results. The product was a phenanthrene *hydrocarbon*, $C_{18}H_{18}$, m. p. 102°, which yielded a *quinone*, m. p. 160·5—161·5°, and a *quinoxaline*, m. p. 154—154·5°, and was oxidised by alkaline potassium ferricyanide to a *phenanthrenedicarboxylic acid*, $C_{16}H_{10}O_4$, isolated as its *methyl* ester, m. p. 136°. In view of the fact that totarol contains a methyl group in position 1, and of the elimination of propane during the dehydrogenation of the alcohol, it seems probable that this hydrocarbon is a 1-methyl-*x*-*iso*propylphenanthrene, but it is different from the three isomers known at present. It is also clear that an alkyl migration must occur either during the transformation of totarol into totarane or during the dehydrogenation:

The research is being actively pursued and the structural problem will be reviewed in a subsequent communication.

EXPERIMENTAL.

Totarol.—The crude alcohol was purified by distillation and by crystallisation of the fraction, b. p. 205—239°/10 mm., from ligroin. It crystallised in clustered needles, m. p. 132°, and had $[\alpha]_D^{20°} + 41{\cdot}34°$ in 4% alcoholic solution (Found: C, 83·9; H, 10·4. Calc. for $C_{20}H_{30}O$: C, 83·9; H, 10·5%). An 11·11% solution of totarol in quinoline ($d_{4°}^{24{\cdot}6°}$ 1·0819, $n_D^{24{\cdot}6°}$ 1·6168) had $d_{4°}^{24{\cdot}6°}$ 1·0778, $n_D^{24{\cdot}6°}$ 1·6110 and an 8·38% solution in acetophenone ($d_{4°}^{24{\cdot}6°}$ 1·02495, $n_D^{24{\cdot}6°}$ 1·5313) $d_{4°}^{24{\cdot}6°}$ 1·0264, $n_D^{24{\cdot}6°}$ 1·5337, whence $[R_L]_D = 87{\cdot}63$ (in quinoline) and 88·98 (in acetophenone). $C_{20}H_{30}O|\overline{\underline{3}}$ requires $[R_L]_D$ 88·08. With perbenzoic acid, the alcohol absorbed oxygen equivalent to 3·15, 3·15 ethylene linkages.

Totaryl Formate.—A mixture of totarol (5 g.) and 98% formic acid (60 c.c.) was boiled for 2 hours, poured into ice-water, neutralised with dilute sodium hydroxide solution, and extracted with ether. The residue obtained by evaporating the dry solution was recrystallised from alcohol, which deposited hexagonal prisms, m. p. 125·5° (Found: C, 79·95; H, 9·35. $C_{21}H_{30}O_2$ requires C, 80·3; H, 9·55%).

Totaryl Acetate.—Concentrated sulphuric acid (2 drops) was added to a solution of totarol (19·2 g.) in acetic anhydride (148 c.c.), and the mixture boiled for 1 hour. Acetic anhydride was destroyed by warming with water, and the precipitate recrystallised from ethyl alcohol. The *acetate* consisted of rectangular plates, m. p. 121·5° (Found: C, 80·3; H, 9·8. $C_{22}H_{32}O_2$ requires C, 80·5; H, 9·75%), and had $[\alpha]_D^{18°} + 44{\cdot}58°$ in 4% solution in ether. Hydrolysis with 10% methyl-alcoholic potash afforded totarol, so no isomerisation had been caused by the acid reagents.

Totaryl Hydrogen Phthalate.—Totarol was heated at 140° for 6 hours with an equal weight of phthalic anhydride. The mixture was extracted with ether, and the extract filtered to remove phthalic anhydride and shaken with sodium hydroxide solution. The solid obtained on acidification was extracted with chloroform, filtered from undissolved phthalic acid, and recrystallised from alcohol. *Totaryl hydrogen phthalate* was obtained in small prisms melting somewhat indefinitely at 161—163° (Found: C, 77·0; H, 7·5. $C_{28}H_{34}O_4$ requires C, 77·4; H, 7·8%). Hydrolysis with 2*N*-alcoholic potash afforded totarol.

Totaryl Methyl Ether.—Methyl iodide (40 c.c.) was added to a suspension of potassium totaryl oxide, prepared from the metal (2·4 g.), totarol (7·2 g.), benzene (140 c.c.), and xylene (70 c.c.) heated at 70° for 2 hours, and the mixture boiled for 2 hours. Alcohol (20 c.c.) was then added, and the mixture diluted with a large volume of ether. The solution was washed, dried, and evaporated. Recrystallisation from chloroform–ethyl alcohol afforded small rhombs, m. p. 92—92·5°, $[\alpha]_D^{18°} + 41{\cdot}95°$ (4% solution in ether), of *totaryl methyl ether* (Found: C, 83·7; H, 10·3. $C_{21}H_{32}O$ requires C, 84·0; H, 10·7%). Yield, 82%. With perbenzoic acid, the ether absorbed oxygen equivalent to 2·95 and 2·85 ethylene linkages.

Reduction of Totarol.—Totarol and totaryl acetate in acetic acid or alcohol could not be reduced in presence of Adams's platinum oxide catalyst at 20—70° and at pressures up to 3 atmospheres. Palladium–strontium carbonate also was ineffective as a catalyst, but reduction was smoothly effected in presence of 10% palladium–charcoal. The alcohol (4·8 g.) in acetic acid (50 c.c.) was shaken with hydrogen in the presence of palladium–charcoal (1·6 g.), 1045 c.c. (2·8 mols.) of hydrogen being absorbed in 6 hours at 70° at a pressure of 30 lb. per sq. in. (at atmospheric pressure, the same quantity of hydrogen is absorbed after 36 hours at 70—80°). The hot solution was filtered, the solvent removed by distillation under diminished pressure, and the residue dissolved in the minimum quantity of ethyl acetate. The solution deposited an impure hydrocarbon, m. p. 80—82°, and recrystallisation from methyl alcohol furnished thick plates of *totarane* (2·5 g.), m. p. 74·5—75° (Found: C, 86·7; H, 12·9. $C_{20}H_{36}$ requires C, 87·0; H, 13·0%). The hydrocarbon gave no colour with tetranitromethane and had $[\alpha]_D^{20°} - 31{\cdot}06°$ in 4% ethereal solution. Evaporation of the ethyl acetate afforded *dihydrototarol* (1·6 g.), which crystallised from ligroin in clustered plates, m. p. 151—151·5°, $[\alpha]_D^{20°} + 20{\cdot}13°$ in 4% ethereal solution (Found: C, 83·1; H, 10·9. $C_{20}H_{32}O$ requires C, 83·3; H, 11·1%). This alcohol gave a pale yellow colour with tetranitromethane and when digested with formic acid afforded *dihydrototaryl formate*, which crystallised from methyl alcohol in plates, m. p. 104·5—105° (Found: C, 80·0; H, 10·2. $C_{21}H_{32}O_2$ requires C, 79·8; H, 10·1%).

Tetrahydrototarol.—Dihydrototarol was not reduced in ethyl alcohol or ethyl acetate at 70° and 2 atmospheres in presence of palladium–charcoal, but reduction took place in acetic acid. A mixture of dihydrototarol (1·0 g.), palladium–charcoal (0·3 g.) and acetic acid (50 c.c.) was shaken in hydrogen until absorption ceased, filtered hot, and evaporated under diminished pressure. A hot saturated solution of the residue in ethyl acetate deposited a little dihydrototarol and crystallisation of the soluble portion from ligroin furnished elongated rectangular prisms of *tetrahydrototarol*, m. p. 134·5° (Found : C, 82·3; H, 11·7. $C_{20}H_{34}O$ requires C, 82·7; H, 11·7%). This compound gave a faint yellow colour with tetranitromethane.

Dehydrogenation of Totarol.—(i) *With selenium.* Totarol (15 g.) and selenium powder (30 g.) were heated at 310—320° for 34 hours and the cold mixture was dissolved in acetone, boiled with charcoal, and evaporated. The residue was dissolved in hot sodium hydroxide solution, filtered, and reprecipitated with acid. Recrystallisation from benzene afforded small clustered needles, m. p. 190—191° (Found : C, 86·3; H, 5·85. $C_{15}H_{12}O$ requires C, 86·5; H, 5·7%). The mother-liquors were diluted with ether and washed with alkali, and the solution dried and evaporated. Distillation of the residue from sodium afforded a colourless oil (0·6 g.), b. p. 155—160°/4 mm., which soon solidified. The crude hydrocarbon was purified by conversion into its picrate and warming with ammonia. The regenerated hydrocarbon (0·02 g.) melted at 118° and, when mixed with picric acid (0·02 g.) in alcohol, furnished a picrate which melted at 134·5° either alone or after admixture with authentic 1-methylphenanthrene picrate. The same hydrocarbon (0·14 g.) was also obtained by heating a mixture of the phenol $C_{15}H_{12}O$ (0·5 g.) with zinc dust (13 g.) and allowing the vapours to pass through a 20 cm. layer of hot zinc dust. The hydrocarbon and its picrate did not depress the m. p.'s of 1-methylphenanthrene and its picrate.

(ii) *With sulphur.* A mixture of totarol (3 g.) and sulphur (3 g.) was heated at 180—260° for 5 hours and then distilled at 4 mm. In this way, 1·2 g. of the phenol, m. p. 190—191°, were obtained, but no appreciable quantity of hydrocarbon was produced.

(iii) *Catalytic.* A mixture of totarol (3 g.) and 10% palladium–charcoal (2 g.) was heated for 6¼ hours at 310—330° and for 3 hours at 350—360°. The volume of gas evolved was 1245 c.c. and 0·4 g. of the phenol $C_{15}H_{12}O$ and 0·04 g. of 1-methylphenanthrene (picrate, m. p. 133·5°) were isolated from the residue.

Investigation of the Phenol $C_{15}H_{12}O$.—Methylation of the phenol (0·2 g.) with sodium hydroxide (0·15 g.), water (1 c.c.), and methyl sulphate (0·5 c.c.) at 60° furnished a *methyl* ether, which crystallised from alcohol in white plates, m. p. 133·5—134·5° (Found : C, 86·2; H, 6·5. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%). When the phenol (0·3 g.), acetic anhydride (3·4 g.), and sodium acetate (0·1 g.) were boiled for 1 hour, the *acetate*, m. p. 133·5—136°, was obtained in 87% yield (Found : C, 81·4; H, 5·6. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%). Oxidation of the acetate (0·5 g.) in acetic acid (7·5 c.c.) with chromic anhydride (0·6 g.) in water (1 c.c.) and acetic acid (2·5 c.c.) at 50—60° furnished an orange-yellow *quinone*, which crystallised from glacial acetic acid in rhombic plates, m. p. 207° (decomp.) (Found : C, 72·7; H, 4·9. $C_{17}H_{12}O_4$ requires C, 72·85; H, 4·3%). The quinone (0·133 g.) in the minimum amount of acetic acid and *o*-phenylenediamine (0·062 g.) in alcohol (1·5 c.c.) afforded a *quinoxaline*, which separated from alcohol–chloroform in long yellow needles (0·13 g.), m. p. 244·5—245·5° (Found : C, 78·65; H, 4·65. $C_{23}H_{16}O_2N_2$ requires C, 78·4; H, 4·5%) The acetoxy-quinone (0·02 g.) was hydrolysed by trituration with 2*N*-aqueous alcoholic sodium hydroxide, and the product precipitated with acid and recrystallised from alcohol. The *hydroxy-quinone* separated in small clustered needles, m. p. 228° (decomp.) (Found : C, 75·2; H, 4·5. $C_{15}H_{10}O_3$ requires C, 75·6; H, 4·2%). The hydroxy-quinone formed a deep indigo-blue solution in dilute aqueous potassium hydroxide, but the colour remained unchanged on warming. The phenol $C_{15}H_{12}O$ did not depress the m. p. of synthetic 7-hydroxy-1-methylphenanthrene and there was no depression when the respective acetates and methyl ethers were mixed.

Dehydrogenation of Totarane.—This hydrocarbon was recovered unchanged after heating at 310—320° for 18 hours with selenium. Dehydrogenation of totarane (0·9 g.) with 10% palladium–charcoal for 4 hours at 300—340° afforded 420 c.c. of gas and extraction of the residue with ether furnished a crystalline *hydrocarbon*, which was purified through its picrate and crystallised from alcohol in thick plates (0·15 g.), m. p. 101·5—102° (Found : C, 92·3; H, 7·4. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). The *picrate* crystallised from alcohol in golden-yellow needles, m. p. 142·5° (Found : C, 62·3; H, 4·7. $C_{18}H_{18},C_6H_3O_7N_3$ requires C, 62·2; H, 4·5%). Oxidation of the hydrocarbon (0·2 g.) in acetic acid (3 c.c.) with chromic anhydride (0·26 g. in 0·5 c.c. of water and 1·5 c.c. of acetic acid) at 50—60° afforded the *quinone*, which crystallised in long rods, m. p. 160·5—161·5° (Found : C, 81·5; H, 6·1. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%). The *quinoxaline* separated from alcohol–chloroform in clusters of rods, m. p. 154—154·5° (Found : C, 85·8; H, 6·1; N, 8·3. $C_{24}H_{20}O_2$ requires C, 85·7; H, 5·9; N, 8·3%).

Oxidation of the Hydrocarbon $C_{18}H_{18}$.—The hydrocarbon (2·5 g.) was stirred at 90° with a solution of potassium ferricyanide (500 g.) and potassium hydroxide (38 g.) in water (1·25 l.). After 30 and 60 hours, further amounts of oxidising agent (200 g. and 100 g.) and alkali (35 g. and 18 g.) were added and the reaction was continued for another 20 hours. The cold liquid was filtered, and the salts extracted with ether to recover unchanged hydrocarbon (0·6 g.). The aqueous solution was acidified with dilute sulphuric acid and extracted with ether for 48 hours. The ethereal solution was extracted with dilute alkali and the brown amorphous precipitate (0·2 g.; m. p. 140—150°) obtained on acidification was shaken with cold methyl alcohol. The soluble acid had m. p. 177—179° and the insoluble portion, m. p. 200—206°. These acids were dissolved in ether and esterified with diazomethane. The ester of the acid of higher m. p. solidified after 48 hours, but that from the acid, m. p. 177—179°, remained oily. The solid ester was fractionally crystallised from methyl alcohol. The first crop of crystals (1) consisted of small needles, m. p. 135—136°, and the second (2) of clustered needles, m. p. 135·5—136°, both of which were analysed [Found: (1) C, 74·2; H, 5·5; (2) C, 73·6; H, 5·0. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·7%].

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