CVII.—*Constituents of* Myoporum Lætum, *Forst.* (The " Ngaio "). *Part II. Hydrogenation of Ngaione and Ngaiol and Dehydration of Ngaiol.*

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THE presence of two double bonds in ngaione (J., 1925, 2200) has now been confirmed by the process of hydrogenation with Paal's colloidal palladium. Both ngaione and ngaiol, the secondary alcohol obtained from it by reduction, take up four atoms of hydrogen to form saturated *tetrahydro*-derivatives, $C_{15}H_{26}O_3$ and $C_{15}H_{28}O_3$. Tetrahydrongaione was characterised by the crystalline *picrolonate*

of *tetrahydrongaiylamine*, obtained from the ketone by reduction of its liquid oxime.

Attempts to obtain a dioxide from ngaione- and tetrahydrongaione-hydrazones by the methods of Woulff and Kishner have been unsuccessful.

The action of dehydrating agents on ngaiol has been exhaustively investigated. Concentrated formic acid at the boiling point gave a 50% yield of *ngaiol formate* [compare citronellol, which by this treatment gives citronellol formate almost quantitatively (Schimmel & Co., Report, 1901, 47), and caryophyllene, which with formic acid gives the formate of caryophyllene alcohol (Robertson, Kerr, and Henderson, J., 1925, **127**, 1944)]. On treatment with potassium hydrogen sulphate, ngaiol loses a molecule of water, to form *dehydro-ngaiene dioxide*,* $C_{15}H_{22}O_2$, but the yield is not large. *Ngaiylamine* was prepared from ngaioneoxime by reduction with sodium and alcohol, and converted into the phosphate. This, on dry distillation in a vacuum according to the method of Harries (*Annalen*, 1903, **328**, 91), yielded no product. Dilute aqueous (2N), 50% aqueous, and 10% alcoholic sulphuric acid caused racemisation and a slow change to a dehydrated compound, while complete resinification took place with 50% alcoholic sulphuric acid at 60—70° and with 80% aqueous sulphuric acid at 0°. This is in marked contrast to the behaviour of calameone, $C_{15}H_{26}O_2$, which easily loses two molecules of water when boiled for $\frac{1}{2}$ hour with 10% aqueous sulphuric acid (Thoms and Beckström, *Ber.*, 1902, **35**, 3187). The best method of obtaining dehydrongaiene dioxide is by the action of alcoholic potash on the unstable *chloride*, formed by the action of thionyl chloride and pyridine on ngaiol.

Dehydrongaiene dioxide has a molecular refractivity correspond-ing to the presence of three double bonds, and with colloidal palladium takes up three molecules of hydrogen, yielding *tetrahydro-ngaiene dioxide*, $C_{15}H_{28}O_2$. The remarkable stability of two of the oxygen atoms in ngaiol to the action of dehydrating agents lends strong support to the conclusion that they are oxidic in character. They are not immune, however, from attack by oxidising agents, and it is hoped in a later publication to describe their behaviour on oxidation.

If Skita's colloidal palladium or platinum be used instead of Paal's palladium for the hydrogenation of ngaiol, the product con-tains a considerable proportion of a *glycol*, $C_{15}H_{30}O(OH)_2$, evidently formed through fission of one of the oxide rings by the hydrogenat-ing agent. Since no trace of such a compound has been obtained

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* The nomenclature is based on the hypothetical sesquiterpene, ngaiene, $C_{15}H_{24}$, corresponding to ngaione.

in the course of numerous experiments with Paal's colloid, it seems probable that the formation of the glycol is due to the slight acidity of Skita's reagent.

EXPERIMENTAL.

(a) *Hydrogenation.*—The hydrogen burette used was modelled on that of Francke (*Chem. Ztg.*, 1913, **37**, 958), the leading-tubes through rubber bungs being replaced by direct seals to a calibrated, thick-walled glass tube of about 5 cm. bore. The shaking-bottle was an ordinary 750 c.c. reagent bottle fitted with a hollow, ground-glass stopper joined to a tap and leading-tube, and held in by a clamp which gripped the top shoulder of the stopper.

The following modifications considerably decreased the tendency of the catalyst to become poisoned and lose its activity. During the preliminary evacuation, and also during the hydrogenation, alcohol vapour is drawn up and condenses in the rubber tubing; on the introduction of the hydrogen stream, this flows back into the hydrogenation bottle, carrying with it minute particles of rubber. A small inverted Kjeldahl trap was inserted on the leading-tube above the tap to prevent the reflux of any liquid that had been in contact with rubber, and a plug of cotton wool was inserted above the bulb to remove particles of rubber from the hydrogen stream. In default of a flexible copper connexion (Skita, *Ber.*, 1912, **45**, 4594), these precautions were found to ensure fairly regular results. Small particles of rubber were apt to be carried back from the side-tube of the receiver during the distillation at low pressure previous to hydrogenation. This defect was remedied by the use of a small Kjeldahl trap and a plug of glass wool in the side-tube of the external receiving tube.

Tetrahydrongaione. A suspension of ngaione (10 g., fractionally distilled at reduced pressure, and distilled again from a metal-bath immediately before use) in 100 c.c. of 50% ethyl alcohol was treated with a solution of Paal's colloidal palladium containing 0·05 g. of metal, and shaken with hydrogen at $1\frac{1}{2}$ atm. pressure. The rate of absorption decreased steadily from the beginning, and several additions of fresh colloid were required during the course of the experiment. In the best circumstances, one molecular proportion was absorbed in $2\frac{1}{2}$ hours, and further shaking for 10 hours completed the reaction. It was usually necessary, however, to extract and redistil the oil and to hydrogenate it with fresh colloid at least once before complete saturation could be reached. *Tetrahydrongaione* was obtained in 80% yield as a colourless, odourless oil, b. p. 196—198°/29 mm., $d_{20°}^{20°}$ 0·9977, $[\alpha]_D - 5·41°$, $n_D^{20°}$ 1·4652; $[R_L]_D$ 70·42 (calc. for $C_{15}H_{26}O_3$: $[R_L]_D$ 70·38) (Found : C, 70·6; H, 10·4.

$C_{15}H_{26}O_3$ requires C, 70·8; H, 10·3%). No trace of tetrahydro-ngaiol was observed in the product of hydrogenation.

The p-*nitrophenylhydrazone* and *oxime* were prepared as viscous liquids. The *semicarbazone* slowly crystallised to a waxy mass, but could not be recrystallised. Tetrahydrongaione oxime was therefore converted by reduction with sodium and alcohol into *tetrahydrongaiylamine*, a colourless, limpid oil with a strong odour, b. p. 198—200°/29 mm., $d_{20°}^{20°}$ 0·968, $n_D^{20°}$ 1·4718, $[R_L]_D$ 73·82 (calc. for $C_{15}H_{29}O_2N$: $[R_L]_D$ 73·78) (Found : C, 70·1; H, 11·6; N, 5·5. $C_{15}H_{29}O_2N$ requires C, 70·5; H, 11·5; N, 5·5%). *Tetrahydro-ngaiylamine picrolonate* was prepared in alcoholic solution and separated, after three crystallisations from alcohol, in bright yellow prisms, m. p. 184—185° (Found : N, 13·7. $C_{25}H_{37}O_7N_5$ requires N, 13·5%).

Dihydrongaiol. Ngaiol, purified through the acid phthalate (see Part I, *loc. cit.*), was treated as above described, the reaction being interrupted after the absorption of one molecule of hydrogen. Repeated distillation of the resulting oil yielded *dihydrongaiol*, a colourless, odourless oil, b. p. 199—202°/28 mm., $d_{20°}^{20°}$ 1·0009, $[\alpha]_D$ — 11·73°, $n_D^{20°}$ 1·4702, $[R_L]_D$ 70·86 (calc. for $C_{15}H_{26}O_3|_1^=$: $[R_L]_D$ 71·41) (Found : C, 70·9; H, 10·6; M, cryoscopic in benzene, 254. $C_{15}H_{26}O_3$ requires C, 70·8; H, 10·3%; M, 254). Acetylation yielded a *monoacetate*, a light yellow oil, b. p. 192°/29 mm., $d_{20°}^{20°}$ 1·0152, $n_D^{20°}$ 1·4631, $[R_L]_D$ 80·42, saponification value (by direct titration after saponification with absolute alcoholic potash), 186 ($C_{15}H_{25}O_2\cdot OAc|_1^=$ requires $[R_L]_D$ 80·78; S.V. 189).

Tetrahydrongaiol, the product of complete saturation of ngaiol with hydrogen under the above conditions, was obtained as a colourless, almost odourless, viscous oil, b. p. 202—206°/29 mm., $d_{20°}^{20°}$ 0·9917, $[\alpha]_D$ + 2·96°, $n_D^{20°}$ 1·4674, $[R_L]_D$ 71·76 (calc. for $C_{15}H_{28}O_3$: $[R_L]_D$ 71·88) (Found : C, 70·2; H, 11·0; M, cryoscopic in benzene, 264. $C_{15}H_{28}O_3$ requires C, 70·3; H, 11·0%; M, 256). The product was free from glycol (see hydrogenation with Skita's reagent, later). Reduction of tetrahydrongaione with sodium and alcohol gave tetrahydrongaiol with physical constants almost identical with those recorded. The phenylurethane was obtained as a viscous syrup which did not crystallise even after removal of all adhering oil by distillation in steam.

Tetrahydrongaiol slowly decolorised aqueous potassium perman-ganate, but was quite unaffected by bromine in aqueous ether. Acetylation with acetic anhydride yielded *tetrahydrongaiol acetate*, a colourless oil with a slightly sharp odour, b. p. 205°/29 mm., $d_{20°}^{20}$ 1·0096, $n_D^{20°}$ 1·4615, $[R_L]_D$ 81·06, saponification value, 184 (calc. for $C_{15}H_{27}O_2\cdot OAc$: $[R_L]_D$ 81·25; S.V. 187).

An attempt was made to prepare a di- or tri-acetate of tetrahydrongaiol by boiling this (2 g.) with freshly-distilled acetyl chloride (10 g.). The excess of acetyl chloride was then decomposed with sodium bicarbonate, and the oil was extracted with ether, and freed from solvent in a vacuum at 100° (Saponification value of the residual brown liquid, 200. Calc. for tetrahydrongaiol monoacetate, 194). The substance distilled at 1 mm. pressure without decomposition (unchanged refractive index) as a light yellow liquid, $n_D^{20°}$ 1·4682, $d_{20°}^{20°}$ 0·9973. A trace of chlorine was present (Found : C, 68·9; H, 10·3. $C_{15}H_{27}O_2 \cdot OAc$ requires C, 68·4; H, 10·2%). These results show that only a *monoacetate* had been formed, and that no dehydration had taken place (compare calameone, which by this treatment loses two molecules of water). The physical constants of the acetate obtained by this method indicate a considerable amount of isomerisation by the strongly acid reagent.

The glycol produced by hydrogenation of ngaiol. Ngaiol (10 g.) in 250 c.c. of 60% alcohol was shaken with colloidal platinum (prepared by inoculation of 10 c.c. of a 1% solution of chloroplatinic acid with colloidal palladium according to the method of Skita) at 2 atm. pressure. Two successive treatments yielded a colourless, viscous oil, which proved on fractionation to be a mixture of mono- and di-hydroxy-compounds.

Fraction I had b. p. 185—200°/21 mm., $d_{20°}^{20°}$ 0·9768, $n_D^{20°}$ 1·4664 (Found : C, 69·8; H, 11·4; *M*, by Rast's camphor method, 261. $C_{15}H_{28}O_3$ requires C, 70·3; H, 11·0; *M*, 256. $C_{15}H_{30}O_3$ requires C, 69·7; H, 11·7%; *M*, 258). The acetate was prepared in the usual way with acetic anhydride, extracted with ether, and freed from ether in a vacuum at 100°. The light yellow oil thus obtained had saponification value 240. The fraction was therefore evidently a mixture of tetrahydrongaiol with an oxido-glycol.

Fraction III consisted of a fairly pure *oxido-glycol*, b. p. 217—220°/21 mm., $d_{20°}^{20°}$ 0·9734, $n_D^{20°}$ 1·4668, $[R_L]_D$ 73·58 {calc. for $C_{15}H_{28}O(OH)_2$: $[R_L]_D$ 73·96} (Found : C, 69·7; H, 11·8; *M*, by Rast's camphor method, 250. $C_{15}H_{30}O_3$ requires C, 69·7; H, 11·7%; *M*, 258). The acetate, prepared as described above, was an almost colourless oil, $n_D^{20°}$ 1·4550, saponification value 304 [$C_{15}H_{28}O(OAc)_2$ requires S.V. 326].

(b) *Action of Halogens and Halogen Acids.*—Ngaione and ngaiol are very sensitive to the action of halogens and halogen acids. When treated with iodine monochloride according to the Wijs method, ngaione gave the iodine value 101, and ngaiol the value 104, corresponding very closely to the theoretical values, 102 and 104, respectively, for the presence of one double bond. This failure of the Wijs method to give a correct indication of the extent of un-

saturation is not unusual with constituents of essential oils, but it is of interest that in each of the above cases one double linking is so definitely indicated.

Bromine water was only slowly decolorised, whereas bromine in cooled chloroform was rapidly absorbed by ngaione, giving a black tar, with evolution of much hydrogen bromide. Bromine in hydroxylic solvents, such as ether–alcohol (1 : 1) at $-10°$, and glacial acetic acid, was rapidly decolorised by ngaione, and hydrogen bromide was then copiously evolved, even before the addition of one molecule of bromine was completed. The instability of the bromine addition compounds, especially in wet solvents, would account for the slow rate of decoloration of bromine water by ngaione and ngaiol. A crystalline bromide, or even a liquid compound with the bromine content of a dibromide, was not obtained in any of the above experiments.

When gaseous hydrogen bromide or hydrogen iodide was passed into their cooled glacial acetic acid solutions, ngaione and ngaiol were rapidly and completely resinified. The action of halogen acids on tetrahydrongaione and tetrahydrongaiol will be described in a later paper.

(c) *Hydrazones of Tetrahydrongaione and Ngaione.*—It has been shown by Woulff (*Annalen*, 1912, **394**, 86) and by Kishner (*Chem. Zentr.*, 1912, I, 1713 ; 1913, I, 706 ; *et al.*) that the carbonyl group of many ketones can be replaced by a methylene group by decomposition of their hydrazones (see also Staudinger, *Ber.*, 1911, **44**, 2197).

Tetrahydrongaione easily formed a hydrazone when heated in alcoholic solution for 6 hours with an excess of 90% hydrazine. Removal of the extracting ether in a vacuum at $100°$ yielded a thick, colourless oil, $n_D^{20°}$ 1·4920. This decomposed to a considerable extent on distillation, with much evolution of gas, the residue being presumably a ketazine. The distillate had b. p. 210—220°/13 mm. and $n_D^{20°}$ 1·4921 (Found : N, 9·9. $C_{15}H_{26}O_2{:}N{\cdot}NH_2$ requires N, 10·4%). The low value for nitrogen was probably due to the presence of a trace of ketazine. In subsequent experiments, no attempt was made to purify the hydrazone.

When tetrahydrongaionehydrazone was heated at 120—180° with a small lump of fused caustic potash or with platinised tile (Kishner, *loc. cit.*), some evolution of nitrogen took place ; no oil was obtained volatile in steam, and it was evident that the reaction had stopped at the formation of the ketazine, a very viscous oil which did not crystallise after 6 months' standing.

Tetrahydrongaionehydrazone was decomposed by alcoholic sodium ethoxide in a sealed tube at 160—165°, and at 190—200°, giving an

inflammable gas, ammonia, and substances of approximate composition $C_{12}H_{22}O$ or $C_{14}H_{26}O$. Ngaionehydrazone under the same conditions formed a complex mixture of decomposition products, b. p. 120—210°/29 mm. The low-boiling portion had an odour resembling that of citral, whilst a fraction, b. p. 170—190°/29 mm., gave analytical values (C, 79·1; H, 11·2%) of no obvious meaning.

It is clear that the hydrazones are decomposed by sodium ethoxide with loss of carbon from the molecule, possibly owing to the presence of an oxide linking next to the carbonyl group. That this change is not wholly related to the oxide rings, but is an intrinsic property of the hydrazone, was shown by the fact that ngaiol remained completely unaltered, even as regards its specific rotation, when heated for 12 hours with alcoholic sodium ethoxide in a sealed tube at 160—170°.

The results suffice to show that it is not possible to obtain by this method the dioxides $C_{15}H_{24}O_2$ and $C_{15}H_{28}O_2$ from ngaione and tetrahydrongaione, respectively. The investigation of the reaction has therefore been left in abeyance until more is known of the structure of ngaione.

(d) *Action of Dehydrating Agents on Ngaiol.*—(1) *Concentrated formic acid.* Ngaiol (20 g.) was heated on the water-bath with 90% formic acid (70 g.) for 5 minutes. The acid was then neutralised with sodium carbonate, and the oil extracted with ether. Distillation gave 11 g. of a light yellow oil, b. p. 186—188°/26 mm., $d_{20}^{20°}$ 1·0387, $n_D^{20°}$ 1·4751 (Found : C, 69·5; H, 9·0; saponification value, 162. $C_{15}H_{23}O_2 \cdot O \cdot COH$ requires C, 68·5; H, 8·7%; S.V., 200. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·6%). The oil was thus a mixture of ngaiol and its formate, from which ngaiol was recovered with unchanged physical constants by saponification with alcoholic potash. Heating of ngaiol for $\frac{1}{2}$ hour with 100% formic acid caused almost complete resinification.

(2) *Potassium hydrogen sulphate.* An intimate mixture of ngaiol (1 part) and the finely-powdered dehydrating agent (2 parts) was rapidly heated to 190° in an atmosphere of carbon dioxide. After $\frac{1}{4}$ hour, the product was cooled, and distilled in steam. Extraction of the distillate with petrol gave a 40% yield of a mixture of about equal parts of ngaiol and *dehydrongaiene dioxide*, $C_{15}H_{22}O_2$. The latter was separated by fractional distillation as an orange-coloured oil with a somewhat tarry odour, b. p. 168—174°/29 mm., $d_{20}^{20°}$ 0·9689, $n_D^{20°}$ 1·4914, $[R_L]_D$ 70·03 (calc. for $C_{15}H_{22}O_2|_{3}^{=}$: $[R_L]_D$ 68·95). The high value of the molecular refraction may be due to the presence of conjugated double bonds (Found, for two different specimens : C, 76·2, 76·4; H, 9·6, 9·3. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%). The substance rapidly absorbed oxygen from the air, forming a thick brown oil.

(3) *Treatment with zinc dust.* It has been shown by Semmler (*Ber.*, 1894, **27**, 2520; 1900, **33**, 776) and others (Gaudurin, *Ber.*, 1908, **41**, 4361; Ruzicka and Stoll, *Helv. Chim. Acta*, 1924, **7**, 100) that many alcohols are reducible by means of zinc dust at a high temperature. Ngaiol, however, was completely unaffected when heated with three times its weight of zinc dust at 210—220° in a sealed tube in an atmosphere of carbon dioxide, and even when heated at 250—260° for 4 hours it suffered no change other than slight decreases in the density and the optical rotation. No pressure was developed in the tube in either case.

(4) *Dry distillation of the amine phosphate.* Ngaione oxime was unaffected by sodium amalgam and acetic acid (compare Goldschmidt, *Ber.*, 1887, **20**, 486), but was easily reduced by sodium and alcohol, giving a 70% yield of *ngaiylamine*, a colourless, limpid, strongly odorous liquid which gradually turned brown in the air, b. p. 184—186°/29 mm., $d_{20}^{20°}$ 0·9940, $[\alpha]_D$ — 18·63°, $n_D^{20°}$ 1·4822, $[R_L]_D$ 72·07 (calc. for $C_{15}H_{23}O_2 \cdot NH_2|_{?}^{=}$: $[R_L]_D$ 72·64) (Found : C, 71·4; H, 10·2; N, 5·6. $C_{15}H_{25}O_2N$ requires C, 71·6; H, 10·0; N, 5·6%). The amine was unstable to hot hydrochloric acid, but the double compound with platinic chloride could be prepared in the cold as a bright yellow solid, decomp. 170—180° [Found : Pt, 21·4. $(C_{15}H_{23}O_2 \cdot NH_2)_2, PtCl_4$ requires Pt, 21·4%].

Ngaiylamine hydrobromide was obtained pure, by several crystallisations from a cold concentrated solution in absolute alcohol by addition of dry ether, in long, white, rectangular prisms, m. p. 190—191° (Found : Br, 24·1. $C_{15}H_{25}O_2N$,HBr requires Br, 24·1%). Unlike the hydrochloride, it is not hygroscopic.

Benzenesulphonngaiylamide was prepared by the Schotten–Baumann process, and the resulting oil extracted with ether. The substance crystallised in elongated, rectangular prisms, m. p. 107—108° [Found : N (micro-Kjeldahl), 3·5. $C_{21}H_{29}O_4NS$ requires N, 3·6%].

Ngaiylamine picrolonate was obtained as a yellow powder, which formed amber-coloured prisms in radiating tufts on recrystallisation from warm absolute alcohol; m. p. 162—163°, independent of the rate of heating (Found : N, 14·0. $C_{25}H_{33}O_7N_5$ requires N, 13·6%).

(5) *Treatment with sulphuric acid.* Ngaiol (6 g.) was boiled with 2N-sulphuric acid (40 g.) for 1 hour, and recovered, by distillation in steam, without appreciable change in physical constants other than a 50% lowering of the specific rotation. Boiling with 33% sulphuric acid for 6 hours produced a resin, and also a substance, b. p. 182—189°/29 mm., $d_{20}^{20°}$ 1·0008, $n_D^{20°}$ 1·4802 (Found : C, 73·8; H, 9·5. Ngaiol, $C_{15}H_{24}O_3$, requires C, 71·4; H, 9·6%). A certain amount of

dehydration had thus taken place, but the product was impure, and the yield was small.

(6) *Dehydrongaiene dioxide prepared through ngaiyl chloride.* For the preparation of ngaiyl chloride, the Darzens process (*Compt. rend.,* 1911, **152**, 1314; Forster and Cardwell, J., 1913, **103**, 1341) was chosen as the most suitable in view of the sensitiveness of the ngaiol molecule to halogen acid (see p. 735). To a mixture of ngaiol (10·6 g.) and pure dry pyridine (3·6 g.; 1 mol.), thionyl chloride (5·4 g.; 1 mol.) was added slowly with shaking and cooling in ice. After standing for 1 hour at room temperature, the yellow product was decomposed by heating it on the water-bath for 1 hour, and the resulting oil was acidified and extracted with ether. On removal of the solvent a heavy, black, oily *chloride* was obtained which was very unstable, partly decomposing even at water-bath temperature. Distillation at 16 mm. pressure caused much decomposition with evolution of hydrogen chloride, and the distillate contained only 3% of chlorine (calc. for $C_{15}H_{23}O_2Cl$: Cl, 13·1%). The oil was therefore heated for 2 hours with N-alcoholic potash, and the product distilled in steam. The main portion of the resulting liquid, a yellow oil with a tarry odour, boiled at 170—175°/28 mm., $d_{30°}^{20°}$ 0·9751, $[\alpha]_D - 10·84°$, $n_D^{20°}$ 1·4854, $[R_L]_D$ 68·90 (calc. for $C_{15}H_{22}O_2|\frac{=}{3}$: $[R_L]_D$ 68·95) (Found : C, 76·7; H, 9·5. Calc. for $C_{15}H_{22}O_2$: C, 76·9; H, 9·5%). The yield was 45% of the theoretical. (Dehydrongaiene dioxide must be prepared and kept in an atmosphere of carbon dioxide, or other indifferent gas, since it easily absorbs oxygen from the air.)

iso*Dehydrongaiene Dioxide.*—Ngaiol can also be converted into a dehydrongaiene dioxide by the use of an excess of pure dry quinoline, instead of the calculated quantity of pyridine. The formation of an *iso*-compound under these conditions may be due to the fact that the solution never becomes acid—during the decomposition on the water-bath of the complex thionyl compound described above, the resulting ngaiyl chloride is partly decomposed with evolution of hydrogen chloride.

Quinoline (20 g.; 5 mols.) was mixed with ngaiol (9·3 g.; 1 mol.) at − 15° in a flask through which a stream of dry carbon dioxide was passing, and thionyl chloride (3·1 g.; 1 mol.) was slowly added. After 1 hour, the yellow product was decomposed by heating it on the water-bath for 1 hour, and the chloride present was then further decomposed by the excess of quinoline by heating the mixture at 150—160° for 1 hour. The product was poured into dilute acetic acid and distilled in steam in a current of carbon dioxide. From the resulting oil, which still contained a small quantity of chlorine, a fraction (1 g.) was isolated, free from chlorine, b. p. 168—174°/

29 mm., $n_D^{20°}$ 1·4801, $d_{20°}^{20°}$ 0·9654, $[R_L]_D$ 68·95 (calc. for $C_{15}H_{22}O_2|\frac{=}{3}$: $[R_L]_D$ 68·95) (Found : C, 76·8; H, 9·6. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%). The physical constants indicate that the substance is an isomeride of the dehydrongaiene dioxide obtained by the use of pyridine, probably differing from it in the position of the double bond. The higher-boiling fraction consisted for the most part of unchanged ngaiol.

Tetrahydrongaiene Dioxide.—Dehydrongaiene dioxide (5·9 g.) (obtained by the pyridine method), in presence of Paal's colloidal palladium (7 c.c. of 1% solution) and 50% ethyl alcohol (100 c.c.), absorbed hydrogen only slowly, and several treatments were necessary before saturation was reached. Eventually a colourless oil was obtained, with a slight pineapple odour, b. p. 170—180°/29 mm., $d_{20°}^{20°}$ 0·9379, $n_D^{20°}$ 1·4631, $[R_L]_D$ 70·63 (calc. for $C_{15}H_{28}O_2$: $[R_L]_D$ 70·35) (Found : C, 74·9; H, 11·7. $C_{15}H_{28}O_2$ requires C, 74·9; H, 11·7%).