CCCXXXIV.—*The Chemistry of Aromadendrene. Part I.*

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During the course of his investigations, the late H. G. Smith recorded the presence of a sesquiterpene fraction in the oils obtained from about 140 species of the genus *Eucalyptus* (Baker and Smith, " A Research on the Eucalypts," Sydney, 1920, pp. 336—348), and he expressed the opinion (*op. cit.*, p. 417; *Proc. Roy. Soc. New South Wales*, 1901, **35**, 124) that aromadendrene is the only sesquiterpene present in eucalyptus oils. The largest amounts of aromadendrene were obtained from the oils of *E. nova-angelica* and *E. hæmastoma*, but a considerable quantity was also found to be present in those of *E. Dawsoni*, *E. eximia*, *E. trachyophloia*, *E. affinis*, *E. Maclurata*, *E. cebra*, *E. viminalis*, and *E. acmenoides*. It is probable that this sesquiterpene occurs in the oils of other genera, and it has been suggested tentatively that it is present in those obtained from *Angophora lanceolata* (Smith, *op. cit.*, pp. 17, 418), *Pinus Lambertiana*, Dougl. (Schorger, *U.S. Dept. of Agric. Forest Serv. Bull.*, 1913, No. 119), *Hypericum perforatum*, L. (Zellner, *Arch. Pharm.*, 1925, **263**, 161), *Leptospermum flavescens var. grandiflorum*, Bentham (Penfold, *Proc. Roy. Soc. New South Wales*, 1920, **54**, 198), *L. odoratum*, Cheel (*idem, ibid.*, p. 205), *L. flavescens*, Smith (*idem, ibid.*, 1921, **55**, 171), *L. ericoides* (Johnson and Short, *Rep. Austr. Assoc. Sci.*, 1923, **16**, 220), *L. scoparium* (Short, *J. Soc. Chem. Ind.*, 1926, **45**, 96T), and *L. lanigerum*, Smith (Penfold, *Proc. Roy. Soc. New South Wales*, 1926, **60**, 79).

No solid derivatives of aromadendrene have hitherto been obtained, and for its identification it has been necessary to rely upon the physical constants and upon certain colour reactions, such as that produced by bromine in acetic acid solution. The same colour reactions are, however, exhibited by several dicyclic sesquiterpenes (*e.g.*, gaujene and eudesmene), so they are of very little diagnostic value.*

The purest specimen of aromadendrene isolated by Smith (*op. cit.*, pp. 46, 416) was obtained from the oil of *E. nova-angelica* and had the following physical constants: b. p. 124—125°/10 mm., $[\alpha]_D$ $+4{\cdot}7°$, $n_D^{20°}$ 1·4964, $d_{15°}^{15°}$ 0·9222, $[R_L]_D$ 64·89 (calc. for a dicyclic sesquiterpene, 66·14; for a tricyclic sesquiterpene, 64·40). Semmler ("Ätherischen Öle," 1906, II, 530) suggested that aromadendrene is not an individual substance but possibly consists of a mixture of di- and tri-cyclic sesquiterpenes. In view of Semmler's criticism, and owing to the fact that no derivatives of aromadendrene had been obtained, it was impossible to establish definitely its identity with the sesquiterpene obtained by one of us (*loc. cit.*) from *Leptospermum* oils until further knowledge of the chemistry of aromadendrene had been acquired; such an investigation has now been made possible by the kindness of Mr. A. R. Penfold, Curator of the Technological Museum, Sydney, who supplied us with 1 lb. of an authentic sample of the oil of *E. nova-angelica*.

The sesquiterpene fraction of this oil was repeatedly fractionated in a vacuum over sodium–potassium alloy, a Widmer column being employed. The fractionation was controlled by determination of the refractive indices and optical rotations of the fractions, rather than by observation of the boiling ranges. After about twenty distillations, the sesquiterpene fraction was collected in two main fractions (representing about 20% of the original oil) and their physical constants (see p. 2527) pointed to the conclusion that the bulk of the sesquiterpene fraction consisted of a single tricyclic sesquiterpene exhibiting an exaltation of approximately one unit in its molecular refractive power. This conclusion has been verified by the preparation of a *dihydroaromadendrene* by exhaustive hydrogenation of the sesquiterpene by the methods of Skita and Paal. Both methods yielded the same result, so that isomerisation during

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* Since the sesquiterpene alcohol eudesmol occurs in many eucalyptus oils, it may be anticipated that some of them will also contain eudesmene.

the hydrogenation is improbable. Since the dihydroaromadendrene also showed an exaltation of one unit in molecular refractive power, it is evident that the exaltation exhibited by the sesquiterpene is due to some structural peculiarity and not to its contamination with dicyclic sesquiterpenes. In this respect aromadendrene resembles the tricyclic sesquiterpenes α-gurjunene (Semmler and Spornitz, *Ber.*, 1914, **47**, 1151) and copaene (Semmler and Stenzel, *ibid.*, p. 2555). It is probable, therefore, that aromadendrene contains either a *cyclo*propane ring conjugated with a double bond (as in sabinene) together with a *cyclo*butane ring, or, less probably, two *cyclo*propane rings.

Attempts to obtain solid addition products (nitrosite, nitrosate, nitrosochloride) from aromadendrene have not been successful. The hydrochloride, having approximately the composition $C_{15}H_{25}Cl$, is a liquid which cannot be distilled in a vacuum without considerable decomposition.

Dehydrogenation of aromadendrene with sulphur yielded a deep blue oil (b. p. 122—165°/12 mm.) from which no naphthalene hydrocarbon could be obtained, although a small quantity of a black picrate (azulene picrate ?) was isolated from it. Aromadendrene therefore resembles the other tricyclic sesquiterpenes, with the exception of copaene (Henderson, M'Nab, and Robertson, J., 1926, 3077), in its inability to yield a naphthalene hydrocarbon on dehydrogenation with sulphur (Ruzicka, Stoll, Liebl, and Pontalti, *Helv. Chim. Acta*, 1923, **6**, 846).

Ozonisation of aromadendrene in acetic acid solution produced a compound, $C_{14}H_{22}O$ (m. p. 80—81°), approximately the same yield (60%) being obtained from each of the fractions above. This substance formed an *oxime* and a *semicarbazone*, and was at first considered to be an aldehyde, since, even when recrystallised to constant m. p., it reduced Tollens's reagent. The reduction, however, must have been due to contamination with traces of an impurity (probably formaldehyde), since the compound was devoid of reducing properties after it had been regenerated from its oxime. Moreover, the oxime did not yield a nitrile when it was digested with acetic anhydride. It therefore appears that the compound $C_{14}H_{22}O$ is a ketone, and we propose to call it *aromadendrone*.

Aromadendrone did not yield an enol-acetate when boiled with acetic anhydride and sodium acetate. This indicates that the carbonyl group is either situated in the side-chain or attached to two quaternary carbon atoms in the nucleus.

The results so far obtained indicate that aromadendrene is a tricyclic sesquiterpene, which probably contains a *cyclo*hexane nucleus with two bridges and is therefore allied in structure to α-santalene (Semmler, *Ber.*, 1910, **43**, 446, 1898) and to longifolene (Simonsen, J., 1923, **123**, 2642). The results of ozonisation clearly show the presence of the group $C{\cdot}C(:CH_2){\cdot}C$.

EXPERIMENTAL.

The fractions referred to on p. 2525 had the following properties : (1) b. p. 121°/10 mm., $[\alpha]_{577}^{20^\circ} - 6{\cdot}1^\circ$, $d_{4^\circ}^{20^\circ}$ 0·9116, $n_{D}^{20^\circ}$ 1·4978, $[R_L]_D$ 65·58; (2) b. p. 121—121·4°/10 mm., $[\alpha]_{577}^{20^\circ} \pm 0^\circ$, $d_{4^\circ}^{17^\circ}$ 0·9157, $n_{D}^{17^\circ}$ 1·4993, $[R_L]_D$ 65·44 [Found, for (1) : C, 88·3; H, 11·8; for (2) : C, 88·2; H, 11·9. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%. $[R_L]_D$ for a dicyclic sesquiterpene, 66·14; for a tricyclic sesquiterpene, 64·40].

In addition to these two fractions a small first-running ($n_{D}^{20^\circ}$ 1·4974, $[\alpha]_{577}^{20^\circ} - 13{\cdot}6^\circ$) and a small fraction (b. p. 124°/10·3 mm., $n_{D}^{20^\circ}$ 1·4989, $[\alpha]_{577}^{20^\circ} + 0{\cdot}59^\circ$) were also obtained.

Hydrogenation.—(1) 12 G. of aromadendrene (fraction 2, freshly distilled over sodium), dissolved in pure methyl alcohol (200 c.c.), were hydrogenated in presence of 0·05% of colloidal palladium (Paal and Gerum, *Ber.*, 1908, **41**, 809) in the apparatus described by Skita and Meyer (*Ber.*, 1912, **45**, 3594), hydrogen from a cylinder being passed at slightly above atmospheric pressure for 20 hours. The product was poured into water, extracted with ether, dried, and distilled over sodium. The hydrogenation was then repeated with a further quantity of colloidal palladium (0·05%) and was found to be complete. The product, extracted in the usual way, was distilled over sodium, and practically the whole passed over at 121—122°/10 mm. (Found : C, 87·2; H, 12·7. $C_{15}H_{26}$ requires C, 87·4; H, 12·6%). *Dihydroaromadendrene* is a colourless oil having $d_{4^\circ}^{17^\circ}$ 0·9014, $n_{D}^{17^\circ}$ 1·4871, $[R_L]_D$ 65·83 (calc. for a tricyclic dihydrosesquiterpene, 64·87).

(2) Aromadendrene (fraction 2) was also exhaustively hydrogenated by Skita's inoculation method (*loc. cit.*). Addition of the inoculating solution to the aromadendrene–platinic chloride mixture and subsequent passage of hydrogen tended to yield a granular rather than a colloidal precipitate, and the hydrocarbon was therefore added after the colloidal condition had been induced. The aromadendrene (10·7 g.) was reduced in presence of colloidal platinum (0·95 g.), water (84 g.), and purified acetic acid (200 c.c.) at an excess pressure of 0·25 atm. Absorption of hydrogen ceased after about 6 hours and no further absorption occurred on the addition of more colloidal platinum. The purified product (Found : C, 87·4; H, 12·6%) had b. p. 115—116°/8—9 mm., $n_{D}^{22^\circ}$ 1·4847, $d_{4^\circ}^{22^\circ}$ 0·8972, $[R_L]_D$ 65·71.

Dehydrogenation.—Aromadendrene (8 g.; fraction 1) and sulphur

(4 g.) were heated together for 4 hours, during which the temperature was slowly raised from 210° to 290° and the evolution of hydrogen sulphide was completed. The reaction mixture was then distilled and purified by redistillation from potassium in a vacuum. The distillate (b. p. 122—165°/12 mm.) was a deep indigo-blue oil, from which no naphthalene hydrocarbon could be isolated (as picrate), but which yielded a trace of a black substance (m. p. 114—116°), possibly identical with eucazulene picrate (Ruzicka and Rudolph, *Helv. Chim. Acta*, 1926, **9**, 118).

Aromadendrone.—A solution of aromadendrene (13 g.) in glacial acetic acid (60 c.c.) was cooled in ice-water and treated with a stream of ozonised oxygen (approx. 14% O_3) until a test portion no longer decolorised a dilute solution of bromine in acetic acid (2·5 hours). The straw-coloured liquid was concentrated under diminished pressure at 50—60° to half its volume, cautiously heated until incipient decomposition was observed, and the flask was then cooled in water to moderate the strongly exothermic reaction which took place. In the first experiments the ketone was recovered by steam-distillation, but it was subsequently found better to pour the cold residue into about six times its volume of ice-water, for the crystalline ketone then separated at once and could be filtered off. The filtrate, on neutralisation, deposited a small quantity (0·55 g.) of an amorphous, white solid which was not further examined. Crystallisation of the crude ketone (11·7 g.) from dilute acetone yielded 5 g. of pure substance, and another 3 g. were obtained by recrystallisation of the fraction of the mother-liquor boiling between 142·5° and 150°/10 mm. (total yield, 61%).

Aromadendrone crystallises in feathery, white needles (m. p. 80—81°) having a characteristic odour, and is very soluble in methyl and ethyl alcohols, chloroform, and acetone. It may be recrystallised from 60% alcohol or from acetone by dilution with water (Found: C, 81·4; H, 10·7; M, cryoscopic in benzene, 208·3, 207·6. $C_{14}H_{22}O$ requires C, 81·6; H, 10·7%; M, 206).

The *oxime* was obtained in almost theoretical yield by the interaction of aromadendrone with twice the theoretical quantities of hydroxylamine hydrochloride and sodium bicarbonate in 95% alcohol (44 hours at 56°). It crystallises in needles (m. p. 103°) from methyl alcohol (Found: N, 6·5, 6·4. $C_{14}H_{23}ON$ requires N, 6·3%).

The *semicarbazone*, m. p. 189·5—190·5° (decomp.), prepared in the usual way, is a microcrystalline powder (from hot methyl alcohol) which is difficult to purify (Found: N, 15·7. $C_{15}H_{25}ON_3$ requires N, 16·0%).

Dehydration of the Oxime.—The oxime was boiled (1·25 hours) with twice its weight of purified acetic anhydride. The dark-coloured product was worked up in the usual way, but yielded fractions of high boiling-point instead of a nitrile.

Aromadendrone and Acetic Anhydride.—The ketone (5 g.), purified acetic anhydride (10 g.), and fused sodium acetate (0·5 g.) were boiled together for $\frac{3}{4}$ hour. The product was cooled, shaken with water, and the crystals which separated were taken up in ether, washed with dilute sodium carbonate, dried, and distilled. Almost the whole passed over at 141—144°/10 mm., and the pure ketone (4 g.) was recovered from this fraction.

One of us (W. F. S.) wishes gratefully to acknowledge the receipt of a grant from the New Zealand Institute which enabled him to purchase the ozoniser and hydrogenation and micro-analytical apparatus. Our thanks are due to the Chemical Society for the loan of a vacuum pump, and to the authorities administering the Duffus Lubecki Fund for a scholarship which enabled one of us (L. H. B.) to participate in this investigation.

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[*Received, July 23rd,* 1928.]