224. *Aromadendrene. Part II.*

By C. B. Radcliffe and W. F. Short.

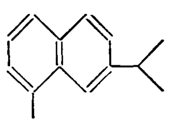
The tricyclic nature of the sesquiterpene aromadendrene has been confirmed by examination of the ketone aromadendrone, $C_{14}H_{22}O$, produced from it by ozonolysis. Dehydrogenation of aromadendrene yields *S*-guaiacazulene. These observations and the frequent association of aromadendrene with eudesmol lead to a provisional formula for the sesquiterpene.

IN Part I (Briggs and Short, J., 1928, 2524) it was concluded that the bulk of the sesquiterpene fraction of the oil of *Eucalyptus nova-angelica* consisted of a tricyclic sesquiterpene (aromadendrene) containing an exocyclic double bond which is probably conjugated with a *cyclo*propane ring. St. Pfau and Plattner (*Helv. Chim. Acta*, **1936**, **19**, 871) consider that the high molecular refraction of the sesquiterpene fraction indicates that it is a mixture of di- and tri-cyclic hydrocarbons. Our conclusion that the main constituent of the sesquiterpene fraction is a tricyclic hydrocarbon was based on the high yield (61%, subsequently raised to 71%) of aromadendrone, $C_{14}H_{22}O$, obtained on ozonolysis and the persistence of the molecular exaltation in dihydroaromadendrene. This has now been confirmed by a further examination of aromadendrone, and we suggest that the name aromadendrene should be reserved for the tricyclic sesquiterpene which affords the solid ketone aromadendrone. The oils of *E. rariflora* and *E. globulus* are now shown to contain aromadendrene associated with at least one other sesquiterpene; after protracted fractionation the maximum yields of aromadendrone were 30% and 37% respectively (see table).

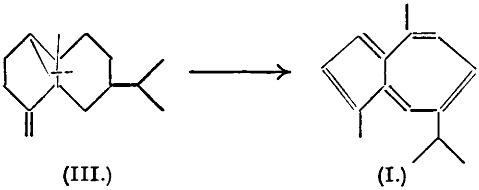
Oxidation of aromadendrene with potassium permanganate affords aromadendrone, *aromadendrene glycol*, $C_{15}H_{26}O_2$, m. p. 118°, which can be further oxidised to aromadendrone, and traces of an acid, m. p. 175—175·5° (decomp.).

The ketone aromadendrone is saturated, since it absorbs only one molecule of hydrogen on catalytic reduction and is reduced by sodium and moist ether to a saturated alcohol, *aromadendrol*, $C_{14}H_{24}O$, which is a mixture of stereoisomerides. It reacts with benzaldehyde to afford a *monobenzylidene* derivative, m. p. 66—66·5°, but is not a methyl ketone, since Fuson's reagent produces no iodoform. Reduction of the oxime of aromadendrone with sodium in ethyl-alcoholic solution gives aromadendrylamine, which is most readily purified through its sparingly soluble *hydrogen oxalate*, m. p. 167—168°. When the corresponding aromadendryltrimethylammonium hydroxide is distilled under diminished pressure, only a trace of hydrocarbon is produced.

Briggs and Short (*loc. cit.*) obtained " azulene " by the dehydrogenation of aromadendrene and St. Pfau and Plattner (*loc. cit.*) obtained *S*-guaiacazulene (I) in 3·6% yield from a sesquiterpene fraction of the oil of *E. globulus*. Repetition of the dehydrogenation of aromadendrene (from *E. nova-angelica*) now gives a higher yield (6·3%) of *S*-guaiacazulene, so this hydrocarbon undoubtedly arises from the tricyclic sesquiterpene. Although aromadendrene is associated with an alcohol of the cadalene type in the oil of *E. globulus* (Ruzicka, Pontalti, and Balas, *Helv. Chim. Acta*, 1923, **6**, 861), it occurs with eudesmol in the majority of the eucalyptus oils and is therefore probably a derivative of eudalene (II). On this basis the provisional formula (III) for aromadendrene is suggested.



(II.)



(III.) (I.)

EXPERIMENTAL.

The sesquiterpene fractions used in these experiments were isolated from the oils by distillation, carefully purified by distillation over sodium, and fractionated with an efficient column. The ozonisations were performed as described in the previous communication.

	Physical constants of sesquiterpene fraction.					Yield of aromadendrone, %.
Source.	B. p./10 mm.	$n_D^{20°}$.	$d_{4°}^{20°}$.	$[R_L]_D$.	α_{5770} (1 dcm.).	
E. rariflora (1)	122—123°	1·4991	0·9122	65·76	+ 1·06°	27
(2)	123—123·5	1·4998	—	—	+ 3·90	26
(3)	125—127	1·5024	0·9197	65·58	+15·68	30
E. globulus (4)	120—121	1·4990	—	—	+ 0·8	37
(5)	123—125	1·4995	0·9159	65·54	+ 2·06	13
(6)	124—125	1·5004	—	—	+ 1·70	8·6

After digestion with 5% alcoholic sulphuric acid at 100° for 12 hours, fraction (5) had $n_D^{20°}$ 1·5026, $d_{4°}^{20°}$ 0·9067, $[R_L]_D$ 65·55.

Aromadendrone.—Recrystallisation from ice-cold methyl alcohol raised the m. p. of this ketone to 84·5—85° (Found : C, 81·55; H, 10·75. Calc. for $C_{14}H_{22}O$: C, 81·6; H, 10·7%). The aromadendrone from fraction (5) had $[\alpha]_{5770}^{16°}$ + 5·75° in 8% alcoholic solution and $[\alpha]_{5770}^{20°}$ + 5·42° (4·8% solution in alcohol) after regeneration from the semicarbazone. The semicarbazone was obtained in two forms. The *α-semicarbazone* crystallised from methyl alcohol in hexagonal plates, m. p. 195—196° (decomp.) (Found : C, 68·5; H, 9·5; N, 15·9. $C_{15}H_{25}ON_3$ requires C, 68·4; H, 9·5; N, 16·0). The *β-semicarbazone* was much less soluble in methyl alcohol, but also crystallised in hexagonal plates, m. p. 201·5—202·5° (decomp.) (Found : C, 68·55; H, 9·5%). The *p-nitrophenylhydrazone* crystallised from ligroin in needles, m. p. 131° (Found : C, 70·5; H, 8·2; N, 12·4. $C_{20}H_{27}O_2N_3$ requires C, 70·4; H, 7·9; N, 12·3%). The ketone (10·3 g.) was recovered unchanged after digestion with alkaline sodium hypobromite (from bromine, 26 g.; water, 800 c.c.; sodium hydroxide, 20 g.) at 100° for several hours. 4·392 Mg. of aromadendrone on hydrogenation in acetic acid with a very active platinum catalyst absorbed 0·51 c.c. of hydrogen at 19·5°/753 mm., equivalent to 0·99 molecule.*

Benzylidenearomadendrone.—A solution of benzaldehyde (11 g.) and aromadendrone (21 g.) in dry benzene was saturated with dry hydrogen chloride at 0° and kept in the ice-chest for 48 hours. The red liquid was poured into ice-water, washed with dilute aqueous sodium carbonate, dried, and boiled for 2½ hours with a solution of sodium (4·8 g.) in absolute alcohol (300 c.c.). The liquid was poured into water, and the oil collected in ether, dried, and distilled. A little aromadendrone was recovered and the *benzylidene* derivative, b. p. 182—197°/1 mm., was purified by crystallisation from methyl alcohol; m. p. 66—66·5° (Found : C, 85·5; H, 8·75. $C_{21}H_{26}O$ requires C, 85·7; H, 8·8%). Yield, 50%.

Aromadendrol.—Reduction of aromadendrone with sodium (8 atoms) in moist ether afforded *aromadendrol*, b. p. 139—140°/10 mm., which solidified to a mass of long needles with a rose odour. The crystals, m. p. 54—59°, had a waxy texture and were too soluble for satisfactory recrystallisation (Found : C, 80·3; H, 11·5. $C_{14}H_{24}O$ requires C, 80·8; H, 11·5%). *Aromadendrol* gave no coloration with tetranitromethane and absorbed no hydrogen when dissolved in acetic acid and shaken with an active platinum catalyst for 3 days.*

Oxidation of Aromadendrene.—Addition of 8% aqueous potassium permanganate (equiv. to 4 atoms of oxygen) during 16 hours to a vigorously stirred emulsion of aromadendrene (20 g., fraction 5) in water at 0—5° furnished unchanged sesquiterpene (2·5 g.), aromadendrone (6 g.), and a mixture of acids (6 g.). The last contained oxalic acid (m. p. 99°; equiv., 62·3; oxalo-*p*-toluidide, m. p. and mixed m. p. 270·5—271°) and a small quantity (0·2 g.) of an *acid* which gave a sparingly soluble sodium salt. The acid separated from ligroin in white crystals, m. p. 175—176° (decomp.) (Found : C, 69·6; H, 10·0. $C_9H_{14}O_2$ requires C, 69·2; H, 10·3%). When half the above amount of potassium permanganate was used, 8 g. of sesquiterpene were recovered, the quantity of the other products was reduced, and an additional neutral product (2·2 g.), b. p. 145—158°/3—4 mm., was obtained. The last, *aromadendrene glycol*, crystallised from light petroleum (b. p. 50—60°) in long rods, m. p. 118° (Found : C, 75·4; H, 10·8. $C_{15}H_{26}O_2$ requires C, 75·6; H, 10·9%). The glycol dissolved in warm 10N-sulphuric acid, but the solution soon became turbid. On oxidation with potassium permanganate in acetone solution it afforded aromadendrone.

Aromadendrylamine.—Reduction of aromadendroxime with sodium (9 atoms) in boiling absolute alcohol furnished the amine in 72% yield. The crude base afforded, with excess of aqueous oxalic acid, a sparingly soluble *hydrogen oxalate*, which crystallised from water in fine needles, m. p. 164—165° (Found : C, 64·8; H, 8·9; N, 4·6. $C_{16}H_{27}O_4N$ requires C, 64·65; H, 9·1; N, 4·7%). Aromadendryltrimethylammonium iodide was obtained by adding methyl iodide (27·5 g.) to a well-shaken mixture of the base (8 g.), sodium hydroxide (7·7 g.), and water (16 c.c.) at 40°. The iodide separated and, after the mixture had stood for 2 days, was collected, recrystallised from hot water, and converted into the ammonium hydroxide by shaking an aqueous solution with freshly prepared silver oxide for 10 hours. The filtered solution was concentrated under diminished pressure, and the residue distilled at 400 mm. Only 0·7 g. of neutral distillate was obtained; the bulk of the hydroxide decomposed in the alternative manner.

Dehydrogenation of Aromadendrene.—A sesquiterpene fraction (b. p. 121°/10 mm., $d_{4°}^{17°}$ 0·9157; $n_D^{17°}$ 1·4993) of the oil of *E. nova-angelica* was dehydrogenated with sulphur as described

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* These determinations were made by Mr. W. F. Boston in the micro-analytical laboratory, Manchester University, by courtesy of Professor I. M. Heilbron.

by St. Pfau and Plattner (*loc. cit.*, p. 869), and the *S*-guaiacazulene isloated as the picrate, m. p. 122°, and identified by conversion into the trinitrotoluene compound, m. p. 89° (Found: C, 61·9; H, 5·6; N, 9·9. Calc. for $C_{15}H_{18},C_7H_5O_6N_3$: C, 62·1; H, 5·4; N, 9·9%).

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