743. *The Volatile Oil of* Pseudowintera colorata. *Part II.*[1] *The Structure of* cyclo*Colorenone.*

By R. E. Corbett and R. N. Speden.

*cyclo*Colorenone, a sesquiterpene ketone present in the volatile oil of *Pseudowintera colorata*, is shown to contain a *cyclo*propane ring, and a constitution is advanced for it.

The volatile oil of *Pseudowintera colorata*, a shrub endemic to New Zealand, was examined by Findlay,[2] who identified β-phellandrene in the terpene fraction, and by Melville and Levi,[3] who identified α-pinene, (+)-limonene, and dipentene, as well as terpene alcohols and esters, and made a preliminary study of the sesquiterpene fraction. By a precise fractional distillation, Corbett and Grant [1] isolated 30 substances from the oil, including a new sesquiterpene ketone, *cyclo*colorenone.

This communication deals with *cyclo*colorenone, $C_{15}H_{22}O$, the highest-boiling of the sesquiterpenoid components. It has also been obtained by chromatography over alumina of the residues remaining in the still-pot. Altogether it represented 7·5% of the total oil. The infrared spectrum showed the presence of a carbonyl group (1698 cm.$^{-1}$), which the ultraviolet spectrum showed to be conjugated with a double bond ($\lambda_{max.}$ 264 mμ, ε 13,260). Some other structural feature extending conjugation was evidently present since there are no simple αβ-unsaturated carbonyl compounds in which $\lambda_{max.}$ is as high as 264 mμ.

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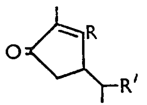
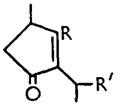
[1] Part I, *J. Sci. Food Agric.*, in the press.
[2] Findlay, *New Zealand J. Sci. Technol.*, 1926, **8**, 107.
[3] Levi and Melville, *J. Soc. Chem. Ind.*, 1932, **51**, 210T.

Hydrogenation of *cyclo*colorenone with Adams catalyst could only be achieved under acid conditions, consumption of hydrogen then ceasing at 3·56 mols., and the product was

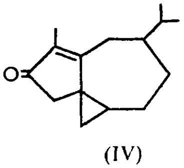

(I)

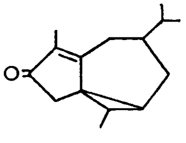

(II)

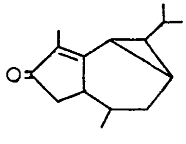

(III)

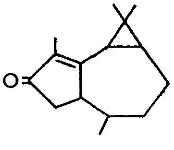
a mixture of hydrocarbons. Hydrogenation at high temperatures and pressures with Raney nickel as catalyst gave a number of products, including a mixture of hydrocarbons, an alcohol, *cyclo*coloranol, $C_{15}H_{26}O$, and a ketone, *cyclo*coloranone, $C_{15}H_{24}O$. Oxidation of *cyclo*coloranol with chromic acid[4] gave *cyclo*coloranone, and confirmed the ketonic nature of the carbonyl function. The same ketone was obtained by reduction of *cyclo*colorenone with lithium in liquid ammonia. This ketone showed no selective ultraviolet absorption attributable to ethylenic linkages, and carbonyl absorption at 1747 cm.$^{-1}$ in the infrared spectrum characterised it as a *cyclo*pentanone. *cyclo*Colorenone is therefore a conjugated *cyclo*pentenone (ethylenic band at 1629 cm.$^{-1}$) and, if it contains only one ethylenic linkage, it must be tricyclic. Reduction of *cyclo*colorenone with lithium aluminium hydride gave *cyclo*colorenol, $C_{15}H_{24}O$, and dehydrogenation of this compound with sulphur gave S-guaiazulene,[5] which established the relative positions of the fifteen carbon atoms in the skeleton. *cyclo*Colorenol was oxidised to *cyclo*colorenone by manganese dioxide. The ready interconversion of these two substances under mild conditions makes the possibility of skeletal or double-bond rearrangement remote. *cyclo*Colorenol showed no ultraviolet maximum above 220 mμ, and its infrared spectrum did not contain any bands in the regions characteristic of the C–H deformation and double-bond stretching vibrations of mono-, di-, or tri-substituted ethylenic linkages. Ethylenic linkages in *cyclo*colorenol and *cyclo*colorenone are therefore tetrasubstituted. Three possible *cyclo*pentenone formulations (I, II, and III), based on an S-guaiazulene skeleton, must thus be considered for *cyclo*colorenone.

A choice between these formulations was made by ozonolysis. Under neutral conditions, this afforded acetic acid, indicative of structure (I) unless some extra complication had been introduced.[6] However the ultraviolet absorption maximum expected[6] for structure (I) would be at 240 ± 5 mμ, and not at the observed wavelength 264 mμ. The latter value is greater than any recorded for a *cyclo*pentenone, but is not sufficiently high for an αβ-γδ-unsaturated ketone based on (I). Such a system of conjugated ethylenic linkages is not feasible in any case, since *cyclo*colorenol has no ultraviolet absorption maximum above 220 mμ. The only other structural feature that could extend conjugation without itself being a chromophore is a *cyclo*propane ring, and structures incorporating this group conjugated with the ethylenic linkage (IV, V, VI, and VII) must therefore be considered for *cyclo*colorenone.


(IV)


(V) (IX*)


(VI) (X*)


(VII) (XI*)

* Saturated hydrocarbon derivatives.

A structure incorporating a *cyclo*propane ring and ethylenic linkage in cross-conjugation with the carbonyl group is not possible, as the ultraviolet spectrum of *cyclo*colorenone

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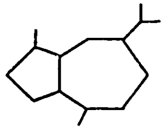
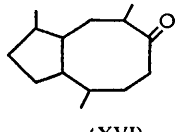
[4] Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2548.

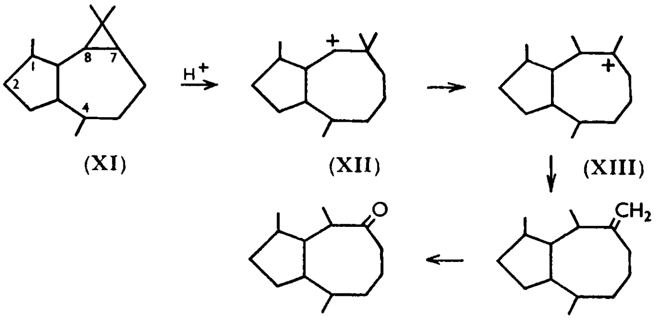
[5] Šorm, Dolejs, Kressel, and Pliva, *Coll. Czech. Chem. Comm.*, 1950, **15**, 83.

[6] Barton and de Mayo, *J.*, 1956, 142.

is not compatible with such a system.[7] Further, the infrared carbonyl absorption of *cyclo*coloranone is consistent with a *cyclo*pentanone, and not a *cyclo*pentanone conjugated with a *cyclo*propane ring.[8]


(VIII)


(XVI)



(XI) (XII) (XIII) (XIV) (XV)

The hydrogenation results with Adams platinum catalyst are explicable on the basis of these structures, since *cyclo*propane rings in conjugation with ethylenic linkages may be unaffected, partially opened, or completely opened on hydrogenation.[9, 10] Structure (IV) is exluded, as the infrared spectra of *cyclo*colorenone and its derivatives do not show a band at 3040—3060 cm.$^{-1}$ (calcium fluoride prism), which has been shown by Cole[11] to be characteristic of the C–H stretching of a CH_2 group in a *cyclo*propane ring. The mixture of saturated hydrocarbons (no light absorption down to 210 mμ) which resulted from the hydrogenation of *cyclo*colorenone was partially soluble (*ca.* 30%) in concentrated sulphuric acid. The insoluble residue $C_{15}H_{28}$, had an infrared spectrum identical with that reported for decahydro-S-guaiazulene (VIII), and physical constants identical with this compound.[12] The compound which dissolved in the sulphuric acid was considered to be a saturated hydrocarbon derived from structure (V, VI, or VII); dissolution in the acid resulted from fission of the *cyclo*propane ring. Confirmation of these views was provided in the following way. The hydrocarbon mixture from the hydrogenation experiment was treated with dry hydrogen chloride, with resultant fission of the *cyclo*propane ring and formation of an exocyclic methylene group (appearance of strong infrared bands at 883 and 1647 cm.$^{-1}$). Ozonolysis of this product gave a ketone, $C_{14}H_{24}O$, together with decahydro-S-guaiazulene. The infrared spectrum of the ketone showed a carbonyl band at 1703 cm.$^{-1}$, corresponding to a *cyclo*heptanone, or a *cyclo*octanone.[13] The saturated hydrocarbon structures corresponding with structures (V, VI, and VII) are designated (IX, X, and XI) respectively. Fission of the *cyclo*propane ring of structure (X) could not lead to a seven- or an eight-carbon ring with an exocyclic methylene group. Likewise fission of the *cyclo*propane ring of structure (IX), while it could lead to a *cyclo*heptane, would almost certainly incorporate a *cyclic* ethylene linkage. Structure (XI) could give rise to an eight-carbon ring system with an exocyclic methylene group.

An explanation of these reactions, based on structure (XI) for the saturated hydrocarbon, and similar to that already advanced by Birch and Lahey[14] to account for the formation of a diketone from *apo*aromadendrone, is given in (XI—XV). Attack by a

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[7] Eastman, *J. Amer. Chem. Soc.*, 1954, **76**, 4115; Barton *et al.*, *J.*, 1958, 963, 688.

[8] Eastman *et al.*, *J. Amer. Chem. Soc.*, 1954, **76**, 4115, 4118; Jones and Herling, *J. Org. Chem.*, 1954, **19**, 1252; Josien and Fuson, *Bull. Soc. chim. France*, 1952, **19**, 389; Wiberley and Bunce, *Analyt. Chem.*, 1952, **24**, 623; Barton and Narayanan, *J.*, 1958, 963.

[9] Kazanskii, Malyshev, Aleksanyan, and Sterin, *Chem. Abs.*, 1957, **51**, 4960; *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1956, 1102.

[10] Kierstead, Linstead, and Weedon, *J.*, 1952, 3610.

[11] Cole, *J.*, 1954, 3807, 3810.

[12] Šorm and Pliva, *Coll. Czech. Chem. Comm.*, 1949, **14**, 274.

[13] Šorm, Dolejs, and Pliva, *Coll. Czech. Chem. Comm.*, 1950, **15**, 187.

[14] Birch and Lahey, *Austral. J. Chem.*, 1953, 379.

proton at position 8 in (XI) would lead through a similar chain of reactions to structure (XVI) for the final ketone. The *cyclo*propane ring fission is not in accordance with Markownikoff's rule. In this case steric factors may be the controlling influence, as the resonance polarisation of the ring would in any case be very small. On the other hand, the ring fission is in accordance with Markownikoff's rule, when *cyclo*colorenol is dehydrogenated to yield S-guaiazulene, and when *cyclo*colorenone is hydrogenated to decahydro-S-guaiazulene. In both cases the direction of opening is governed by the presence of the conjugated ethylenic linkage.

Structure (VII) permits an adequate interpretation of all the experimental observations. The molecular refraction of *cyclo*colorenone is 66·96. The value calculated by using bond refractions determined by Vogel[15] is 65·40. The exaltation, 1·56, is comparable with that reported for the αβ-unsaturated ketones α-vetivone (1·5), β-vetivone (1·64), and eremophilone (1·37). The observed molecular refractions of the saturated derivatives of *cyclo*colorenone are also in good agreement with calculated values, *viz.*, *cyclo*coloranone obs. 65·97, calc. 65·848, and *cyclo*coloranol, obs. 67·34, calc. 67·404.

EXPERIMENTAL

Infrared spectra were determined on a Perkin–Elmer spectrophotometer model 12 C, as liquid films, or in the case of solids, in Nujol. Alumina, grade H, supplied by Peter Spence & Sons Ltd., was used for chromatography, and all solvents were purified before use.

cyclo*Colorenone*.—This compound was isolated from the residues remaining in the still-pot after the distillation of the essential oil of *Pseudowintera colorata*,[1] by chromatography on alumina. The residue (12·65 g.), in *n*-hexane (30 c.c.), was introduced on to a column of alumina (350 g.), and developed with *n*-hexane. Paraffinic hydrocarbons were eluted with hexane–benzene (19 : 1) (1 l.), and *cyclo*colorenone (6·15 g.) was eluted with hexane–benzene (9 : 1) (1 l.); it had b. p. 136—138°/5 mm., n_{D}^{20} 1·5270, d_{D}^{20} 1·0026, $[R_L]_{\mathrm{D}}$ 66·96, $[\alpha]_{\mathrm{D}}^{20}$ −400° (*c* 8·75 in EtOH), $\lambda_{\mathrm{max.}}$ 264 mμ (ε 13,260 in EtOH) (Found: C, 82·6; H, 10·05. $C_{15}H_{22}O$ requires C, 82·5; H, 10·15%). cyclo*Colorenone* 2 : 4-*dinitrophenylhydrazone* was scarlet and had m. p. 217—218° after crystallisation from ethyl acetate, $\lambda_{\mathrm{max.}}$ 404 mμ (ε 31,490 in $CHCl_3$) (Found: C, 63·65; H, 6·4; N, 14·05. $C_{21}H_{26}O_4N_4$ requires C, 63·3; H, 6·6; N, 14·05%).

Hydrogenation of cyclo*Colorenone*.—(*a*) A solution of *cyclo*colorenone (9·3 g.) in ethanol (200 c.c.), containing Raney nickel (1·5 g.) was shaken with hydrogen in an autoclave at 190°/120 atm. (final) for 27 hr. (disappearance of ultraviolet absorption maximum). Removal of the catalyst and solvent afforded an oil (7·8 g.), which was chromatographed in hexane (20 c.c.) on alumina (250 g.). Hexane (150 c.c.) eluted a mixture of hydrocarbons (3·2 g.) (Found: C, 87·9; H, 11·75. Calc. for $C_{15}H_{24}$: C, 88·15; H, 11·85%). Elution with hexane–benzene (1 : 1) (50 c.c.) gave cyclo*coloranone* (0·36 g.), b. p. 210° (bath-temp.)/7 mm. (Found: C, 81·4; H, 10·9. $C_{15}H_{24}O$ requires C, 81·75; H, 11·0%). cyclo*Coloranone* 2 : 4-*dinitrophenylhydrazone* formed yellow needles, m. p. 191—193° (from ethyl acetate), $[\alpha]_{\mathrm{D}}^{20}$ −43° (*c* 2·15 in $CHCl_3$) (Found: C, 62·8; H, 6·9; N, 13·7. $C_{21}H_{28}O_4N_4$ requires C, 63·0; H, 7·05; N, 14·0%). From the same chromatogram elution with ether–ethanol (9 : 1) (100 c.c.) afforded cyclo*coloranol* as a viscous oil (2·12 g.), b. p. 200° (bath-temp.)/6 mm., n_{D}^{20} 1·4952, d_4^{20} 0·9614, $[R_L]_{\mathrm{D}}$ 67·34 (Found: C, 81·2; H, 11·75. $C_{15}H_{26}O$ requires C, 81·0; H, 11·8%). cycloColoranol with 3 : 5-dinitrobenzoyl chloride in pyridine–benzene afforded cyclo*coloranyl* 3 : 5-*dinitrobenzoate*, as colourless needles, m. p. 163—165° (from hexane) (Found: C, 63·2; H, 7·05; N, 6·65. $C_{22}H_{28}O_6N_2$ requires C, 63·45; H, 6·8; N, 6·75%).

(*b*) *cyclo*Colorenone (6·1 g.) in ethanol (40 c.c.) containing 3N-hydrochloric acid (0·5 c.c.) was shaken with hydrogen in the presence of Adams catalyst (500 mg.) at atmospheric pressure (3·56 mols. absorbed). After removal of the solvent, the product was percolated in hexane through alumina and distilled; it (5·0 g.) had b. p. 82°/1·5 mm., n_{D}^{20} 1·4793 (Found: C, 86·95; H, 13·52. Calc. for $C_{15}H_{28}$: C, 86·45; H, 13·55. Calc. for $C_{15}H_{26}$: C, 87·3; H, 12·7%). This product showed no light absorption down to 210 mμ.

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[15] Vogel, " A Text Book of Practical Organic Chemistry," Longmans, Green and Co., Ltd., London, 1956, p. 1036.

Decahydro-S-guaiazulene.—The hydrocarbon mixture from the Raney nickel reduction (2·32 g.) was shaken in glacial acetic acid (10 c.c.) and ethanol (25 c.c.) with hydrogen in the presence of Adams catalyst (290 mg.) at atmospheric pressure. 0·4 mol. of hydrogen was consumed. The product (2·1 g.) had b. p. 110°/6 mm., n_D^{20} 1·4827, d_4^{20} 0·8900, $[\alpha]_D^{20}$ −48·02° (Found: C, 87·1; H, 13·1. Calc. for $C_{15}H_{28}$: C, 86·45; H, 13·55. Calc. for $C_{15}H_{26}$: C, 87·3; H, 12·7%). This product showed no light absorption down to 210 mμ. The above product was shaken with concentrated sulphuric acid for 12 hr. and repeatedly extracted with hexane (20 c.c.). The hexane extract was percolated through alumina, and after removal of the hexane, gave decahydro-S-guaiazulene (1·2 g.), n_D^{20} 1·4790, d_4^{20} 0·8850, $[\alpha]_D^{20}$ +9·36° (*c* 1·0 in EtOH) (Found: C, 86·8; H, 13·2. Calc. for $C_{15}H_{28}$: C, 86·45; H, 13·55%). Šorm *et al.*[12] report n_D^{20} 1·4780, d_4^{20} 0·8803.

Oxidation of cyclo*Coloranol.*—*cyclo*Coloranol (1·87 g.) in acetone (30 c.c.) (distilled over potassium permanganate) at 20° was treated with an 8N-solution of chromic acid [chromic oxide (26·7 g.) in concentrated sulphuric acid (23 c.c.) and water (40 c.c.), made up to 200 c.c.], until oxidation was complete (2·1 c.c.). After dilution with water (20 c.c.), the mixture was extracted with ether (3 × 20 c.c.), and the ether solution washed with aqueous sodium carbonate (3 × 100 c.c.) and water (3 × 50 c.c.) and dried (Na_2SO_4). After removal of the ether, the product was absorbed from hexane (30 c.c.) on to alumina (50 g.). Benzene eluted a pale yellow oil, n_D^{20} 1·4911, d_4^{20} 0·9657, $[R_L]_D$ 65·97 (Found: C, 81·8; H, 11·5. Calc. for $C_{15}H_{24}O$: C, 81·75; H, 11·0%), whose infrared spectrum was identical with that of *cyclo*coloranone (CO band at 1747 cm.$^{-1}$).

Reduction of cyclo*Colorenone with Lithium in Liquid Ammonia.*—Lithium (0·63 g.) was dissolved in liquid ammonia (200 c.c.). *cyclo*Colorenone (2·04 g.) in dry ether (50 c.c.) was added during 35 min. After a further 15 min. ammonium chloride was added, the ammonia allowed to evaporate, the residue extracted with ether, and the extract washed with water and dried (Na_2SO_4). Evaporation afforded a brown oil which was absorbed from hexane (20 c.c.) on to alumina (75 g.). Hexane–benzene (4 : 1) eluted *cyclo*coloranone (0·333 g.) (authentic infrared spectrum). The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in yellow needles, m. p. 201—202°, $[\alpha]_D^{20}$ −79° (*c* 2·5 in $CHCl_3$), and had m. p. 198—202° on admixture with the 2 : 4-dinitrophenylhydrazone, m. p. 191—193°, $[\alpha]_D^{20}$ −43° (mixture of stereoisomers), described above.

cyclo*Colorenol.*—To lithium aluminium hydride (0·35 g., 100% excess) in dry ether (50 c.c.) at 0° *cyclo*-colorenone (4·0 g.) in dry ether (60 c.c.) was added during 30 min. (temp. $\not>$10°). After an additional 30 min., the mixture was cooled to 2°, and water was added dropwise. The ethereal solution was filtered from a granular precipitate, which was in turn triturated with further quantities of ether. The filtrate and washings were washed with distilled water (3 × 100 c.c.) and dried (Na_2SO_4). Removal of the solvent gave cyclo*colorenol* (3·8 g.) which crystallised in needles (from hexane), m. p. 92—93°, $[\alpha]_D^{20}$ −132° (Found: C, 81·75; H, 10·75. $C_{15}H_{24}O$ requires C, 81·75; H, 11·0%).

Oxidation of cyclo*Colorenol.*—*cyclo*Colorenol (0·61 g.) was stirred for 2 hr. with a suspension of manganese dioxide (commercial; 5 g.) in carbon tetrachloride (70 c.c.). Filtration and evaporation afforded a light brown oil (0·55 g.) whose infrared and ultraviolet spectra were identical with those of *cyclo*colorenone. It furnished a 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 216—218° after crystallisation (from ethyl acetate).

Dehydrogenation of cyclo*Colorenol.*—*cyclo*Colorenol (0·28 g.) and finely divided sulphur (0·3 g.) were heated in a nitrate bath for 3 hr. at 220—225°, then extracted with hexane. The hexane solution was shaken with concentrated phosphoric acid. The phosphoric acid extract was diluted with distilled water and then re-extracted with hexane. The hexane solution was washed with water, dried (Na_2SO_4), and evaporated to yield an intensely blue oil, $\lambda_{max.}$ 245, 286, 350, 370 mμ (log ε 4·48, 4·67, 3·75, 3·66), $\lambda_{min.}$ 260, 330, 360 mμ (log ε 4·21, 3·65, 3·57), $\lambda_{max.}$ 605, 660, 730 mμ (ε 430, 354, 127), $\lambda_{min.}$ 650, 720 mμ (ε 346, 112), inflexion, 630 mμ (ε 384). The azulene formed a trinitrobenzene compound, black needles, m. p. 150°, undepressed on admixture with the compound of S-guaiazulene.

Ozonolysis of cyclo*Colorenone.*—*cyclo*Colorenone (200 mg.) in chloroform (25 c.c.) was treated with a stream of ozonised oxygen until the ultraviolet absorption maximum had disappeared. Water (25 c.c.) was added, and the mixture distilled. The distillate was neutralised with aqueous sodium hydroxide, the chloroform removed, and the aqueous residue treated with *p*-bromophenacyl bromide in the usual way. Chromatography of the product in hexane on deactivated alumina (20 g.) gave *p*-bromophenacyl acetate (29·6 mg.), as colourless plates, m. p. 83—85° (mixed m. p. 84—86°).

Isomerisation and Ozonolysis of Reduced Hydrocarbon.—The hydrocarbon mixture (2·20 g.) from hydrogenation (*b*) above was treated with hydrogen chloride for 1 hr. at 0°, then kept at 0° overnight. The infrared spectrum then showed strong bands at 883 and 1647 cm.$^{-1}$. The product was washed in hexane (20 c.c.) with saturated sodium carbonate solution (3 × 15 c.c.) and with water, and percolated through alumina. After removal of the solvent, the resultant halogen-free (Beilstein test) hydrocarbon (1·846 g.) in acetic acid (25 c.c.) was ozonised for 3 hr. The ozonide was decomposed by water (70 c.c.) and zinc (3 g.). Ether (50 c.c.) was added and the extract washed repeatedly with aqueous sodium carbonate and with water, dried (Na_2SO_4), and evaporated to an oil (1·248 g.), which was chromatographed in hexane on alumina. Hexane (50 c.c.) eluted decahydro-S-guaiazulene (670 mg.) (Found: C, 86·25; H, 13·2. Calc. for $C_{15}H_{28}$: C, 86·45; H, 13·55%). (Infrared spectrum identical with that reported for decahydro-S-guaiazulene.) From the same chromatogram elution with ether (125 c.c.) gave a *ketone* (366 mg.), b. p. 110°/1·0 mm. (Found: C, 81·1, 80·95; H, 11·2, 11·4. $C_{14}H_{24}O$ requires C, 80·7; H, 11·6%) (infrared spectrum, CO band at 1703 cm.$^{-1}$).

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