THE VOLATILE OIL OF *PSEUDOWINTERA COLORATA* IV. EPICYCLOCOLORENONE

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Summary

Cyclocolarenone has been converted to epicyclocolarenone and both have been dehydrogenated to the same dienone (II).

In Part I of this series¹ evidence was advanced which established that cyclocolarenone had structure (I). The recent report by Büchi and Loewenthal² of

![Structures](image)

the synthesis of epicyclocolarenone and their elucidation of the stereochemistry of this compound and of cyclocolarenone prompts us to report work which we had initiated directed at elucidating the stereochemistry of cyclocolarenone.

When cyclocolarenone was refluxed with ethanolic potassium hydroxide it yielded a crystalline epicyclocolarenone identical with that reported by Büchi and Loewenthal.² That cyclocolarenone and this epimer can differ only at C₁ or C₁₀, and that no other structural change had occurred in the reaction was confirmed by conversion of both compounds to the same dienone (II) by bromination at C₁ with N-bromsuccinimide, and dehydrobromination with dimethylformamide, reactions analogous with those used by Barton and Pinhey³ in the conversion of geigerin acetate into anhydrogeigerin. On the basis of its ultraviolet spectrum (λₘ₉ₐ₉₉ 326 mμ) and infrared bands at 1682 (cyclopentenone) and 1635 and 1555 cm⁻¹ (conjugated ethylenic linkages) this dienone is formulated as (II). From the manner in which the epimerization was effected, which is analogous with the conversion of 1-epideoxygeigerin to deoxygeigerin,⁴ it is clear that epicyclocolarenone must be the C₁ epimer. The dienone (II) is a useful derivative for correlating the C₁ and C₁₀ epimers of cyclocolarenone.

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A second diene was formulated in low yield in the conversion of both epicyclocolorenone and cyclocolorenone to (II). This diene, which analysed for $C_{15}H_{22}O$ is considered to be formed as a result of the opening of the cyclopropane ring, and is formulated as (III) on the basis of its ultraviolet spectrum ($\lambda_{\text{max}}$, 296 nm), and infrared bands at 1693 (cyclopentenone), and 1630 and 1596 cm$^{-1}$ (conjugated ethylenic linkages).

**Experimental**

Melting points are corrected. Infrared spectra were determined as liquid films or in Nujol on a Perkin-Elmer spectrometer model 21. Alumina, grade I (Brockmann) supplied by Merck, was used for chromatography.

**Epicyclocolorenone.**—Cyclocolorenone (3-8 g) was heated under reflux with ethanolic KOH (100 c.c. of 0·5N) for 2 hr, and the cold solution acidified with dil. $H_2SO_4$. After adding water (1000 c.c.), the solution was kept overnight in the ice-chest, and the crystalline product then collected by filtration. A further small quantity of solid was obtained from the filtrate by ethereal extraction. Crystallization from aqueous ethanol gave epicyclocolorenone (1-74 g), m.p. 68-68.5°C, $[\alpha]_D^20$ -198° (c, 6·9 in CHCl$_3$), $\lambda_{\text{max}}$, 253 nm, (c 15,154 in ethanol) (Found: C, 82·3; H, 10·2%. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%). Epicyclocolorenone, 2,4-dinitrophenylhydrazone was red and had m.p. 189°C after crystallization from ethyl acetate, $\lambda_{\text{max}}$, 397·5 nm (c 30,800 in CHCl$_3$) (Found: C, 63·0; H, 6·9; N, 14·3%). $C_{21}H_{26}O_4N_4$ requires C, 63·3; H, 6·6; N, 14·1%.

**Dehydrogenation of Cyclocolorenone.**—Cyclocolorenone (2-00 g) in carbon tetrachloride (30 c.c.) was refluxed on a water-bath with $\beta$-bromosuccinimide (1·78 g). After 10 min the reaction was complete and the solvent was evaporated at 40°C under reduced pressure, yielding a dark viscous oil (2·86 g). Redistilled dimethylformamide (15 c.c.) was added to this oil, and the solution was refluxed for 15 min. A portion of the dimethylformamide (8·0 c.c.) was distilled off under reduced pressure and water (200 c.c.) was added to the cold solution which was extracted with ether (2 x 100 c.c.). The ethereal extract was washed with 2N $H_2SO_4$ (2 x 50 c.c.) and with water, dried (Na$_2$SO$_4$), and the ether removed to give a dark viscous oil (1·8 g) which was immediately dissolved in hexane and the solution chromatographed on alumina (70 g, column length 7 cm). Elution with hexane–benzene (4:1) (1000 c.c.) gave the liquid diene (III) (0·45 g), b.p. 80°C/0·005 mm, $\lambda_{\text{max}}$, 296 nm (c 20,000 in ethanol) (Found: C, 82·2; H, 9·9%. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%). The diene 2,4-dinitrophenylhydrazone was deep purple and had m.p. 218-5°C after crystallization from hexane–benzene, $\lambda_{\text{max}}$, 411 nm (c 30,000 in CHCl$_3$) (Found: C, 63·4; H, 6·6; N, 13·8%). $C_{21}H_{26}O_4N_4$ requires C, 63·3; H, 6·6; N, 14·1%). From the same chromatogram elution with benzene (1000 c.c.) afforded the diene (II) (0·908 g), which crystallized in cream needles from aqueous methanol, m.p. 63°C, $\lambda_{\text{max}}$, 325 nm (c 19,250 in EtOH) (Found: C, 83·0; H, 9·6%. $C_{15}H_{20}O$ requires C, 83·3; H, 9·3%). The 2,4-dinitrophenylhydrazone crystallized from chloroform–benzene in dark purple needles, m.p. 232°C, $\lambda_{\text{max}}$, 433 nm (c 36,310 in CHCl$_3$) (Found: C, 63·5; H, 6·4; N, 14·2%). $C_{21}H_{24}O_4N_4$ requires C, 63·6; H, 6·1; N, 14·1%.

**Dehydrogenation of Epicyclocolorenone.**—Dehydrogenation of epicyclocolorenone (1-0 g) in the manner already described, gave the diene (III) (0·189 g), b.p. 80°C/0·005 mm, $\lambda_{\text{max}}$, 295 nm (c 20,000 in EtOH), and the diene (II) (0·576 g), m.p. and mixed m.p. 63°C.

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