

THE VOLATILE OIL OF *PSEUDOWINTERA COLORATA*

IV. EPICYCLOCOLORENONE

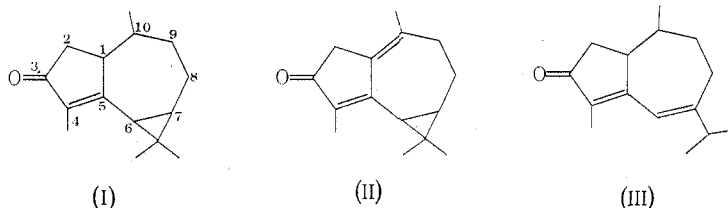
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Summary

Cyclocolorenone has been converted to epicyclocolorenone and both have been dehydrogenated to the same dienone (II).

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



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

When cyclocolorenone was refluxed with ethanolic potassium hydroxide it yielded a crystalline epicyclocolorenone identical with that reported by Büchi and Loewenthal.² That cyclocolorenone 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 (λ_{max} , 326 m μ) 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 epicyclocolorenone must be the C₁ epimer. The dienone (II) is a useful derivative for correlating the C₁ and C₁₀ epimers of cyclocolorenone.

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¹ Corbett, R. E., and Speden, R. N. (1958).—*J. Chem. Soc.* **1958**: 3710.

² Büchi, G., and Loewenthal, H. J. E. (1962).—*Proc. Chem. Soc.* **1962**: 280.

³ Barton, D. H. R., and Pinhey, J. T. (1960).—*Proc. Chem. Soc.* **1960**: 279.

⁴ Barton, D. H. R. *et al.* (1962).—*Proc. Chem. Soc.* **1962**: 112.

A second dienone was formed in low yield in the conversion of both epicyclocolorenone and cyclocolorenone to (II). This dienone, 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 ($\lambda_{\max}$. 296 $m\mu$), 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 $CHCl_3$), $\lambda_{\max}$. 253 $m\mu$, (ϵ 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, $\lambda_{\max}$. 397.5 $m\mu$ (ϵ 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 *N*-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 × 100 c.c.). The ethereal extract was washed with 2N H_2SO_4 (2 × 50 c.c.) and with water, dried (Na_2SO_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 *dienone* (III) (0.435 g), b.p. 80°C/0.005 mm, $\lambda_{\max}$. 296 $m\mu$ (ϵ 20,000 in ethanol) (Found: C, 82.2; H, 9.9%. $C_{15}H_{22}O$ requires C, 82.5; H, 10.2%). The *dienone 2,4-dinitrophenylhydrazone* was deep purple and had m.p. 218.5°C after crystallization from hexane–benzene, $\lambda_{\max}$. 411 $m\mu$ (ϵ 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 *dienone* (II) (0.908 g), which crystallized in cream needles from aqueous methanol, m.p. 63°C, $\lambda_{\max}$. 325 $m\mu$ (ϵ 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, $\lambda_{\max}$. 433 $m\mu$ (ϵ 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 *dienone* (III) (0.189 g), b.p. 80°C/0.005 mm, $\lambda_{\max}$. 295 $m\mu$ (ϵ 20,000 in EtOH), and the *dienone* (II) (0.576 g), m.p. and mixed m.p. 63°C.

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