

THE OCCURRENCE OF LEDOL IN *PHEBALIUM SQUAMEUS* LABILL.*

By F. N. LAHEY† and J. A. LAMBERTON‡

The bark of the tree *Phebalium squameus* Labill., family Rutaceae, known popularly as "Satinwood", contains a crystalline, easily isolated sesquiterpene alcohol, which has been identified as ledol. Ledol was first isolated (Tropp 1875; Hjelt and Collan 1882) from the leaves and flowering tops of *Ledum palustre* L., a member of the family Ericaceae. Through the kindness of Professor N. J. Toivonen and Professor G. A. Nyman of the University of Helsinki, we have been able to compare our material with ledol obtained from that source by Professor Nyman. Hasenfratz (1928) has also reported the occurrence of ledol in *Sphacele parviflora* L., family Labiataeae, but in this instance the identification depends on similarity of properties only.

The physical properties of the ledol from *P. squameus* are in close agreement with those given in the literature, and its identification is based on the mixed melting point determination and comparison of the infra-red absorption spectra. Ledol is a tertiary alcohol, and so readily dehydrated that derivatives cannot be prepared by the usual methods. We have been unable to obtain the crystalline chromate reported by Wienhaus (1914), and the hydrocarbon obtained by formic acid dehydration differs in its optical rotation from that reported by Kir'yalov (1949).

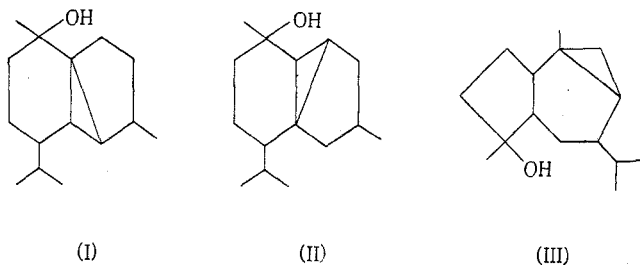
Komppa and Nyman (1938) proposed alternative formulae I and II for ledol, based on the observation that dehydrogenation gave both cadalene and an azulene. Kir'yalov (1953) has made an extensive study of the degradation products of ledol and claimed that formulae I and II were erroneous and that ledol was really 1,4-dimethyl-7-isopropylbicyclo[5,3,0]-1-decalol with a cyclopropane ring between the 4 and 6 positions (III).

* Manuscript received January 11, 1956.

† Chemistry Department, University of Queensland.

‡ Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

Both I and III are in accord with the formation of *S*-guaiazulene from ledol and its derivatives (Nyman and Mikander 1941; Kir'yalov 1953). Formula III, however, is unlikely because the infra-red absorption spectrum of ledol lacks the absorption band in the 3024–3058 cm^{-1} region, which Cole (1954) has found to be characteristic of a cyclopropane having an unsubstituted CH_2 group included in the ring. The presence of a tertiary hydroxyl group is



supported by the existence of a strong absorption band at 1115 cm^{-1} . Zeiss and Tsutsui (1953) found the characteristic C—O stretching frequency in 1-methylcyclohexan-1-ol, for instance, to lie at 1117 cm^{-1} , whereas the corresponding bands for primary and secondary alcohols lie at much lower frequencies.

The evidence for the structure of ledol is therefore inconclusive.

Experimental

Dry, milled bark of *P. squameus* (1.5 kg) was extracted by percolation with cold ether. The oily residue remaining after evaporating the ether was distilled under reduced pressure. After a small forerun of low boiling material, crude ledol (14–15 g) distilled and crystallized. It was purified by crystallization from light petroleum. Alternatively, ledol may be obtained by steam distillation of the material extracted by cold ether or methanol.

Purified ledol (10–11 g) melted at 104–105 °C (uncorr.) and this m.p. was undepressed by admixture with an authentic sample of ledol (m.p. 104–105 °C, uncorr.) from *L. palustre* (Found: C, 80.8; H, 11.8%. Calc. for $\text{C}_{15}\text{H}_{26}\text{O}$: C, 81.0; H, 11.8%). The solution in ethanol has a slight positive rotation, $[\alpha]_{\text{D}}^{20} + 4^\circ$ (c, 2.01 in ethanol). The literature gives: m.p., 105–106.5 °C (Kir'yalov 1949), $[\alpha]_{\text{D}} + 7.98^\circ$ (Hjelt and Collan 1882), $[\alpha]_{\text{D}} + 0.5^\circ$ (Kir'yalov 1949), (10% solution in ethanol).

Ledol has a pleasant smell and a marked tendency to sublime under reduced pressure and on warming, when it forms long needle-shaped crystals. A solution in ethanol showed no measurable ultraviolet absorption. Ledol is very resistant to oxidation. It was recovered unchanged after ozonolysis in acetic acid solution and after heating with potassium permanganate in acetone. It did not give a colour with a solution of tetranitromethane in chloroform.

(a) *Dehydration of Ledol*.—Attempts to prepare derivatives of the alcohol group caused dehydration. Dehydration was carried out in the ways described by Kir'yalov (1949) for the preparation of ledene and leddiene.

(i) Heating ledol with ethanolic sulphuric acid gave a hydrocarbon, b.p. 94–96 °C (1.5 mm), having $[\alpha]_{\text{D}}^{20} + 46^\circ$ (c, 1.94 in ethanol) (Found: C, 87.9; H, 11.8%. Calc. for $\text{C}_{15}\text{H}_{24}$: C, 88.2; H, 11.8%). For ledene, Kir'yalov gives b.p. 110–113 °C (3 mm), $[\alpha]_{\text{D}}^{16} + 48.43^\circ$ (10% solution in ethanol).

(ii) Heating ledol with formic acid gave an isomeric hydrocarbon having b.p. 92–95 °C (1.5 mm); n_{D}^{20} , 1.4973; $[\alpha]_{\text{D}}^{20} - 11.2^\circ$ (c, 2.32 in ethanol) (Found: C, 87.8; H, 11.8%). It gave a blue to purple colour with bromine in acetic acid or chloroform. For leddiene, Kir'yalov gives b.p. 103–104 °C (3 mm); n_{D}^{20} , 1.4971, $[\alpha]_{\text{D}}^{17} + 36.5^\circ$ (10% solution in ethanol).

The authors wish to thank Dr. J. B. Willis for the infra-red spectra measurements.

References

- COLE, A. R. H. (1954).—*J. Chem. Soc.* **1954** : 3807.
HASENFRATZ, V. (1928).—*C.R. Acad. Sci. Paris* **137** : 903.
HJELT, E., and COLLAN, U. (1882).—*Ber. dtsh. chem. Ges.* **15** : 2500.
KIR'YALOV, N. P. (1949).—*J. Gen. Chem. Moscow* **19** : 2123. (*Chem. Abstr.* **43** : 1155.)
KIR'YALOV, N. P. (1953).—*Sbornik Statei Obshchei Khim.* **2** : 1617. (*Chem. Abstr.* **49** : 5389.)
KOMPPA, G., and NYMAN, G. A. (1938).—*C.R. Lab. Carlsberg* **22** : 272.
NYMAN, G., and MIKANDER, G. A. (1941).—*Suomen. Kem. B* **14** : 3.
TROPP, I. (1875).—*Ber. dtsh. chem. Ges.* **8** : 542.
WIENHAUS, H. (1914).—*Ber. dtsh. chem. Ges.* **47** : 330.
ZEISS, H. H., and TSUTSUI, M. (1953).—*J. Amer. Chem. Soc.* **75** : 897.