

## X-Ray Crystallographic Determination of the Structure of a Grindelane Diterpenoid from *Lasiocorys capensis*

By GEOFFREY GAFNER and GERT J. KRUGER

(National Physical Research Laboratory, Council for Scientific and Industrial Research, Pretoria)

and DOUGLAS E. A. RIVETT\*

(Department of Chemistry, Rhodes University, Grahamstown, 6140, South Africa)

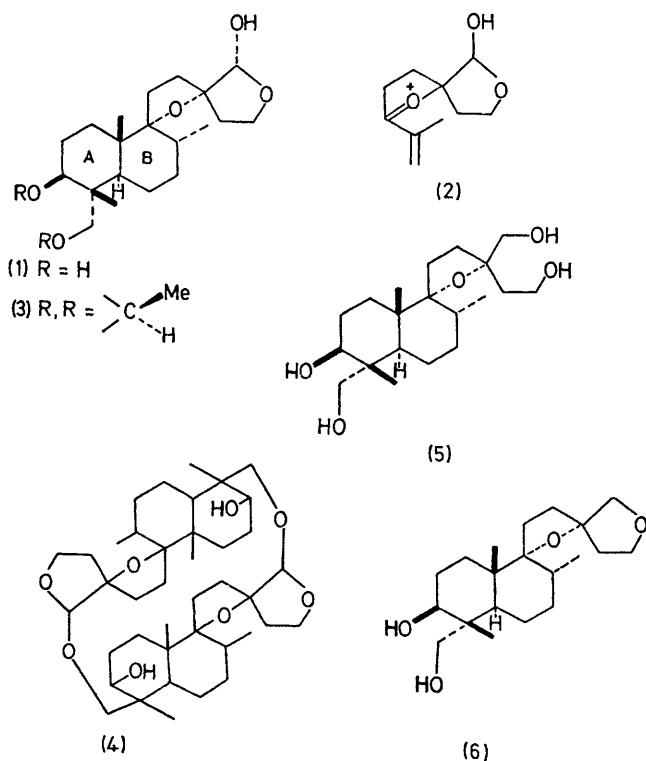
**Summary** Lasiocoryin from *Lasiocorys capensis* (Labiatae) is the first 9,13-epoxylabdane (grindelane) diterpenoid to have its structure elucidated by crystallographic analysis; it forms a novel cyclic dimeric acetal on treatment with acid, and this study makes a minor correction to, but otherwise confirms, the stereochemistry of lagochilin.

LASIOCORYIN,  $C_{20}H_{34}O_5$ , m.p.  $175^\circ$ ,  $[\alpha]_D + 6^\circ$ , which exists in the plant as the acetate, is a bitter principle of *Lasiocorys capensis* (Labiatae) and is shown here to have the structure

(1). Its n.m.r. spectrum revealed the presence of a secondary and a primary hydroxy-group and a hemiacetal ring; there was no carbonyl absorption in its i.r. spectrum. The mass spectrum showed the molecular ion (38%) and the base peak at  $m/e$  183 due to the fragment (2).

Lasiocoryin formed an ethylidenedioxy-derivative (3),  $C_{22}H_{36}O_6$ , m.p.  $152^\circ$ ,  $[\alpha]_D - 34^\circ$ , which was oxidised to a  $\gamma$ -lactone,  $C_{22}H_{34}O_5$ , m.p.  $187^\circ$ ,  $\nu_{max}$   $1790\text{ cm}^{-1}$ . Compound (3) crystallized in the orthorhombic space group  $P2_12_12_1$  with unit-cell dimensions of  $a = 24.87$ ,  $b = 10.38$ ,  $c =$

7.96 Å,  $Z = 4$ ;  $D_c = 1.229$   $D_m = 1.214$  g cm<sup>-3</sup>. A total of 1505 independent reflections were measured on a Philips PW1100 single-crystal diffractometer with graphite-monochromated Mo- $K_\alpha$  radiation. The structure and



relative stereochemistry were determined using the tangent formula.<sup>1</sup> Calculations were performed on an IBM 360/65 computer with the  $X$ -ray system of crystallographic programs.<sup>2</sup> Full-matrix least-squares analysis with isotropic temperature factors for the hydrogen atoms and anisotropic factors for the rest gave a final  $R$  value of 0.059. Carbon-carbon bond-lengths averaged  $1.52 \pm 0.02$ , carbon-oxygen  $1.42 \pm 0.02$ , and carbon-hydrogen  $0.98 \pm 0.09$  Å. No deviations greater than 3 times these standard deviations were found.

Refluxing aqueous ethanolic HCl converted lasiocoryin into a high-melting dimer, C<sub>40</sub>H<sub>84</sub>O<sub>8</sub> (4), m.p. 300° (decomp.),  $[\alpha]_D - 79^\circ$ . The structure of the dimer was determined by  $X$ -ray analysis of its  $p$ -bromobenzoate, C<sub>54</sub>H<sub>70</sub>Br<sub>2</sub>O<sub>10</sub>, m.p. 320° (decomp.), which also crystallized in the space-

group  $P2_12_12_1$  with unit-cell dimensions of  $a = 21.10$ ,  $b = 21.02$ ,  $c = 11.36$  Å,  $Z = 4$ ;  $D_c = 1.369$ ,  $D_m = 1.367$  g cm<sup>-3</sup>. A total of 1710 independent reflections were measured on a Hilger & Watts single-crystal diffractometer using graphite monochromated Mo- $K_\alpha$  radiation. Refinement was stopped at  $R = 0.128$  in favour of determining the structure of the ethylenedioxy-derivative (3), but has been carried far enough to allow a determination of the absolute stereochemistry of lasiocoryin by intercomparison of Bijvoet pairs from the  $p$ -bromobenzoate of the dimer. The chirality is shown in both (1) and the stereodiagram.

Lasiocoryin was reduced by sodium borohydride to a tetraol (5) which crystallized as a monohydrate, m.p. 111–112°, from aqueous ethanol. A structure identical with (5), except for the stereochemistry of the C-17 methyl group, has been proposed by Chizhov *et al.*<sup>3</sup> for lagochilin, m.p. 115–116°, from *Lagochilus inebrians*. Dr Chizhov has kindly compared the tetraol (5) with lagochilin and found them to be identical. With this small revision the structure suggested for lagochilin is thus firmly established.

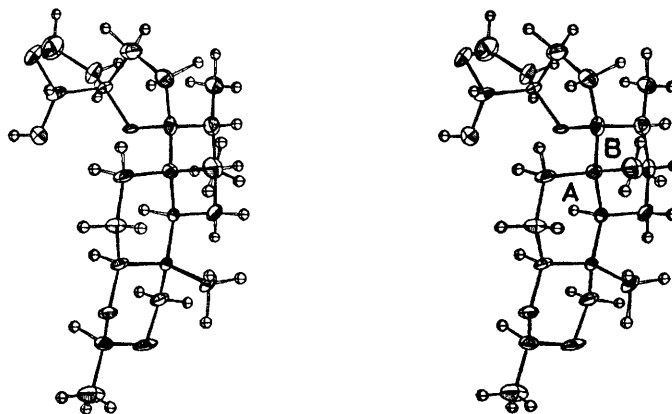


FIGURE. Stereodiagram of the ethylenedioxy-derivative of lasiocoryin.

The cyclic acetal structure of the dimer (4) formed by reaction of the primary hydroxy-group of one lasiocoryin molecule with the hemiacetal group of another, appears to be unique. Similar acid treatment of lagochilin gave anhydrolagochilin (6),<sup>3</sup> m.p. 80–81°. The dimer (4) showed none of the complexing properties of the crown ethers<sup>4</sup> and also had no antibiotic activity.<sup>5</sup>

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<sup>1</sup> J. Karle and H. Hauptman, *Acta Cryst.*, 1956, **9**, 635.

<sup>2</sup> J. M. Stewart, G. J. Kruger, H. Ammon, C. H. Dickinson, and S. R. Hall, 1972, University of Maryland Computer Science Technical Report TR-192.

<sup>3</sup> O. S. Chizhov, A. V. Kessenikh, B. M. Zolotarev, and V. A. Petukhov, *Tetrahedron Letters*, 1969, **17**, 1361; *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1970, **9**, 1983.

<sup>4</sup> C. J. Pedersen, *J. Amer. Chem. Soc.*, 1970, **92**, 391.

<sup>5</sup> We are grateful to Sir Derek Barton for suggesting these tests.