New Metabolites of the Lichen *Buellia canescens* (Dicks.) De Not: Novel Phthalide Catabolites of Depsidones

By TONY SALA and MELVYN V. SARGENT*
(*Department of Organic Chemistry, University of Western Australia, Nedlands, W.A.* 6009, *Australia*)
and JOHN A. ELIX
(*Chemistry Department, Australian National University, P.O. Box* 4, *Canberra A.C.T.* 2600, *Australia*)

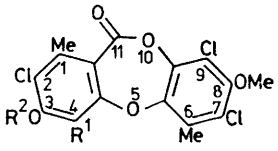
Summary The isolation and structural determination of the lichen metabolites dechlorodiploicin (**2**), dechloro-*O*-methyldiploicin (**3**), buellolide (**4**), and canesolide (**6**) are described; buellolide (**4**) and canesolide (**6**) are thought to arise by catabolism of their congeneric depsidones, in the latter case with Smiles rearrangement.

IN a search for intermediates involved in the biogenesis of depsidones[1] we have subjected an extract of the lichen *Buellia canescens* to a detailed scrutiny. Chromatography of the extract gave the known depsidone diploicin (**1**),[2] two new depsidones dechlorodiploicin (**2**)† and dechloro-*O*-methyldiploicin (**3**), and the unusual phthalides buellolide (**4**) and canesolide (**6**).

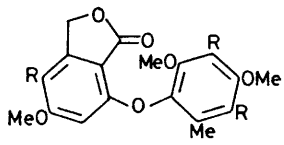
The i.r. spectrum, ν_{max} ($CHCl_3$) 1756 cm^{-1}, of dechlorodiploicin (**2**), m.p. 272·5–274 °C, suggested that it was a depsidone. Its relationship to diploicin (**1**), which has been synthesized by an unambiguous route,[3] was established by methanolysis of the new depsidone to the diaryl ether (**8**), which on hydrogenolysis furnished the dechloro-compound (**9**), identical with the compound obtained from diploicin (**1**) by a similar sequence. That no rearrangement

† All new compounds gave satisfactory elementary analyses or high resolution molecular ion peaks.

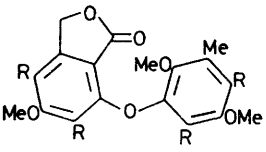
had occurred during the methanolysis of diploicin (**1**), and by analogy, in that of dechlorodiploicin (**2**), was demonstrated by Ullmann synthesis of the diaryl ether (**10**), which was identical to that obtained by methylation of (**9**). The presence, in the ^{1}H n.m.r. spectrum of (**8**), of a high field aromatic proton signal (δ 6·11), suggested that (**8**) was a tri-*ortho*-substituted diaryl ether,[4] and this evidence fixed the positions of the chloro-substituents in dechlorodiploicin (**2**). Dechloro-*O*-methyldiploicin, m.p. 230–231·5 °C, must possess structure (**3**) since it was obtained by methylation of dechlorodiploicin (**2**). The structures of the new depsidones were also confirmed by synthesis.[1]



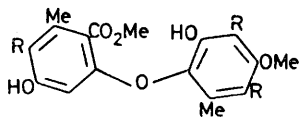
(1) R^1 = Cl, R^2 = H
(2) R^1 = R^2 = H
(3) R^1 = H, R^2 = Me



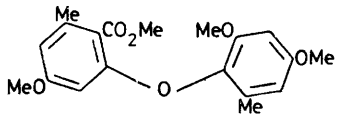
(4) R = Cl,
(5) R = H



(6) R = Cl
(7) R = H

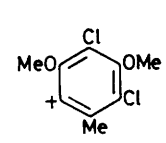


(8) R = Cl
(9) R = H

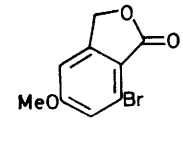


(10)

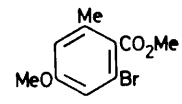
The structure (**4**) of buellolide, m.p. 170–173 °C, was supported by its spectroscopic properties. That it is a phthalide was indicated by its i.r., ν_{max} (CCl_4) 1781 cm^{-1}, and ^{1}H n.m.r. spectra (δ 5·23, 2H, s). The high resolution mass spectrum, in addition to establishing the molecular formula, exhibited peaks at *m/e* **219** (base)/221/223 attributed to the ion (**11**). Hydrogenolysis of buellolide (**4**) gave the diaryl ether (**5**), which like buellolide (**4**), exhibited a high field aromatic proton signal (δ 6·00) in its ^{1}H n.m.r. spectrum, thus fixing the positions of the chloro-substituents. Tridechlorobuellolide (**5**) was synthesized (44%) by Ullmann reaction between the bromo-compound (**12**), obtained by photobromination of compound (**13**)[5] and subsequent hydrolysis, and the phenol (**14**).[6] On treatment with an excess of sulphuryl chloride in dichloromethane compound (**5**) gave buellolide (**4**), identical with the natural product.



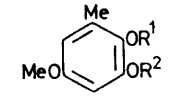
(11)



(12)



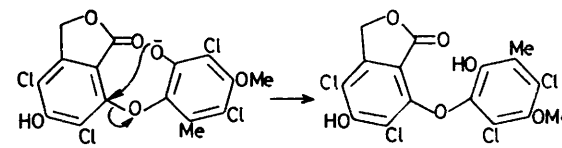
(13)



(14) R^1 = H, R^2 = Me
(15) R^1 = H, R^2 = CH_2Ph
(16) R^1 = Me, R^2 = H

Canesolide (**6**), m.p. 158–160 °C, was very similar in spectroscopic properties to buellolide (**4**), and on hydrogenolysis it gave the diaryl ether (**7**), identical with synthetic material. Methylation and subsequent hydrogenolysis of the phenol (**15**)[3] gave (**16**) which on Ullmann reaction with (**12**) gave tetradechlorocanesolide (**7**) (25%).

Buellolide (**4**) and canesolide (**6**) probably arise biogenetically by catabolism of their congeneric depsidones. Thus dechlorodiploicin (**2**) or *O*-methyldechlorodiploicin (**3**) would undergo fission of the depside linkage, oxidation of the methyl group at the 1-position, and *O*-methylation thus yielding buellolide (**4**). Canesolide (**6**), however, would arise from diploicin (**1**) by a similar sequence but the fission of the depside linkage in this case must be accompanied by a Smiles rearrangement,[7] *e.g.* (**17**)→(**18**).



(17) (18)

We thank the Australian Research Grants Committee for financial support.

(*Received*, 1*st August* 1978; *Com.* 832.)

[1] T. Sala and M. V. Sargent, following communication.
[2] T. J. Nolan, J. Algar, E. P. McCann, W. A. Manahan, and N. Nolan, *Sci. Proc. Roy. Dublin Soc.*, 1948, **24**, 319.
[3] P. Djura, M. V. Sargent, and P. Vogel, *J.C.S. Perkin I*, 1976, 147.
[4] T. M. Cresp, P. Djura, M. V. Sargent, J. A. Elix, U. Engkaninan, and D. P. H. Murphy, *Austral. J. Chem.*, 1975, **28**, 2417 and references therein.
[5] M. V. Sargent, P. Vogel, and J. A. Elix, *J.C.S. Perkin I*, 1975, 1986.
[6] I. M. Godfrey, M. V. Sargent, and J. A. Elix, *J. C. S. Perkin I*, 1974, 1353.
[7] S. Huneck and M. V. Sargent, *Austral. J. Chem.*, 1976, **29**, 1059.