addition products with $Na_2Cr_2O_7$[13], the quinones were identified by their melting points and nuclear magnetic resonance spectra [**2**: m.p. 106-107 °C (102-103 °C, 122.5-123 °C[14,15]); NMR ($CDCl_3$) δ 2.77 (s, 3H, CH_3), 6.92 (s, 2H, 2-, and 3-H's), 7.5-8.3 (m, 3H, 6-, 7-, and 8-H's); GC-MS 172 (M^+, 100%), 157(14), 144(43), 129(3), 118(48), 116(47), 115(54), 90(30), 89(41), 63(21). **3**: m.p. 89-90 °C (90-91 °C[15]); NMR ($CDCl_3$) δ 2.50 (s, 3H, CH_3), 6.93 (s, 2H, 2-, and 3-H's), 7.35-8.05 (m, 3H, 6-, 7-, and 8-H's); GC-MS 172 (M^+, 100%), 157(3), 144(15), 127(12), 118(21), 116(33), 115(52), 90(23), 89(26), 63(18)]. The mass spectrum of the 6-methyl isomer and its retention time relative to 1,4-naphthoquinone were identical to those of the unknown quinone from *P. opilio,* which was on that basis assigned the structure 6-methyl-1,4-naphthoquinone.

Although the defensive secretions of arthropods commonly contain benzoquinones[16], they appear only rarely to contain naphthoquinones. So far only certain tenebrionid beetles have been shown to produce naphthoquinones[17], including (among several 6-alkyl derivatives) 6-methyl-1,4-naphthoquinone, but not 1,4-naphthoquinone itself. There can be no doubt that these substances have a defensive role, at least vis à vis ants. As little as 0.1 µg of either 1,4-naphthoquinone or 6-methyl-1,4-naphthoquinone was found to deter ants (*Formica exsectoides*) from a baited feeding site. Toluquinone and naphthalene were less effective by about 2 orders of magnitude[18].

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[3] T. Eisner, D. Alsop and J. Meinwald, in: Handbook of Pharmacology, vol. 48, ch. 5. Ed. S. Bettini. Springer, Heidelberg, 1978.

[4] M.S. Blum and A.L. Edgar, Insect Biochem. *1,* 181 (1971).

[5] T.H. Jones, W.E. Conner, A.F. Kluge, T. Eisner and J. Meinwald, Experientia *32,* 1234 (1976).

[6] J. Meinwald, A.F. Kluge, J.E. Carrel and T. Eisner, Proc. natl Acad. Sci. USA *68,* 1467 (1971).

[7] C. Estable, M.I. Ardao, N.P. Brasil and L.F. Fieser, J. Am. chem. Soc. *77,* 4942 (1955).

[8] L.F. Fieser and M.I. Ardao, J. Am. chem. Soc. *78,* 774 (1956).

[9] T. Eisner, A.F. Kluge, J.C. Carrel and J. Meinwald, Science *173,* 650 (1971).

[10] T. Eisner, T.H. Jones, K. Hicks, R.E. Silberglied and J. Meinwald, J. chem. Ecol. *3,* 321 (1977).

[11] E. Stenhagen, S. Abrahamson and F.W. McLafferty, in: Registry of Mass Spectral Data. Wiley-Interscience, New York 1974.

[12] H. Hopff and C.W. Rautenstrauch, Chem. Abs. *36,* 1046 (1942).

[13] L.F. Fieser, J. Am. chem. Soc. *70,* 3165 (1948).

[14] J. Herzenberg and S. Ruhemann, Ber. dt. chem. Ges. *60,* 889 (1927).

[15] R.G. Cooke, H. Dowd, and W. Segal, Aust. J. Chem. *6,* 38 (1953).

[16] P.L. Altman and D.S. Dittmer, in: Biology Data Book. Fed. Am. Soc. exp. Biol., Bethesda, Maryland, 1973.

[17] W.R. Tschinkel, J. Insect Physiol. *18,* 711 (1972).

[18] T. Eisner and D. Aneshansley, unpublished results.

The identification of norlobariol, a new lichen constituent from *Xanthoparmelia scabrosa* (Tayl.) Hale

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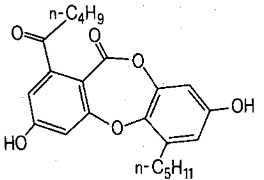
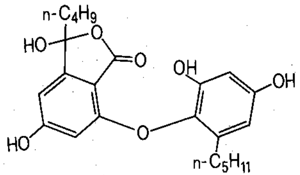
Summary. Norlobariol (I) previously described as a synthetic product derived from norlobaridone (**II**) was isolated as a new metabolite from *Xanthoparmelia scabrosa* (Tayl.) Hale.

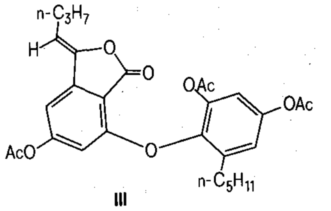
The lichen which was collected from a road side in an industrial part of Lower Hutt, New Zealand, was successively extracted with benzene and acetone. The compound was obtained from the acetone extract by preparative TLC as a brownish solid which was further purified by recrystallization from aqueous methanol to yield colorless needles, m.p. 192-193 °C, λmax (EtOH) 258 and 284 nm and $[\alpha]+12$ °. Its presence could be detected under UV light on silica gel 60 F_{254} TLC plates as a low mobility spot (Rf 0.11) in benzene-dioxane-acetic acid (180:45:5) and as an immobile spot in toluene-acetic acid (20:3). The molecular formula, $C_{23}H_{28}O_7$ was deduced from microanalytical and mass spectral data. The compound gave its highest mass peak at m/e 416 with base peak at m/e 372 together with



II



I



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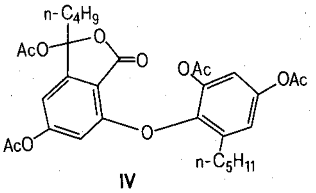
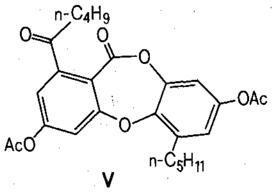


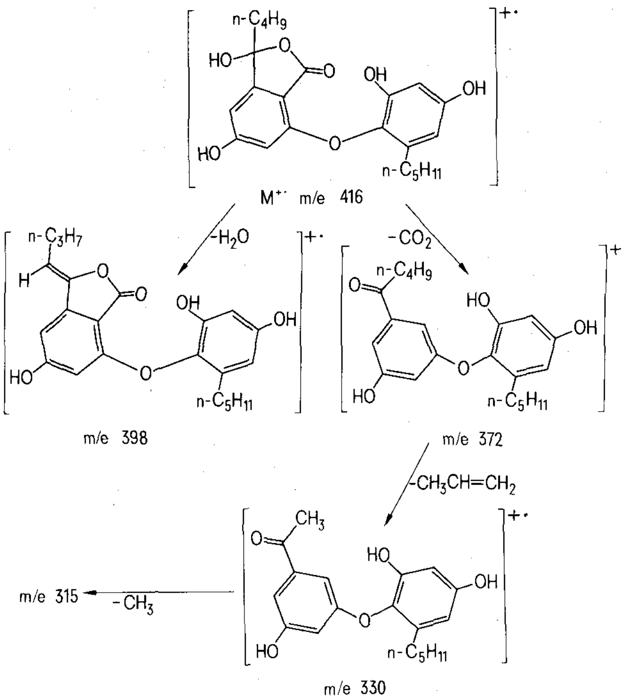
IV



V

Mass spectral data (above m/e 398) of the principal products of acetylation of compound I

Product (R_f value in benzene/acetone 4:1)	m/e (% relative intensity)
III (0.80)	524 (2), 482 (65), 456 (5) 440 (100), 414 (35), 412 (55), 398 (80)
IV (0.60)	584 (5), 542 (3), 525 (5), 524 (3), 560 (3) 482 (100), 458 (5), 440 (100), 412 (30), 398 (30)
V (0.35)	482 (15), 440 (45), 398 (100)



Proposed fragmentation scheme for compound (**I**).

other major fragments at m/e 398, 330 and 315. The TLC and mass spectral data of the compound were identical to those of norlobariol which was obtained by treatment of norlobaridone with hot sodium hydroxide solution. Further, treatment of the compound with boiling formic acid yielded a product which was identical to isonorlobaridone[2]. The NMR (60 MHz) spectrum of the compound in deuterated acetone showed 4 sets of doublets attributable to aromatic protons at δ 6.60 (J, 1.8 Hz, 1 H), 6.42 (J, 2.6 Hz, 1 H), 6.32 (J, 2.6 Hz, 1 H), and 6.07 (J, 1.8 Hz, 1 H) and other signals at δ 2.10 (m, 4 H), 1.30 (m, 10 H), and 0.90 (m, 6 H) which are consistent with the structure of norlobariol. The identity of the lichen metabolite was further confirmed by its inertness to sodium bicarbonate solution and by its reaction with excess diazomethane which yielded a product with the highest mass at m/e 458 thus confirming the presence of 3 phenolic hydroxyls. In addition, acetylation of the metabolite yielded 3 principal products (**III, IV** and **V**) which could be logically explained from the structure of norlobariol. The mass spectral data of the acetylated products are shown in the table. Product (**III**) could arise by the loss of water from (**II**) under the dehydrating conditions of the reaction to yield a triacetylated product, while (**IV**) was the expected tetraacetylated product. Product (**V**) was identical to the product obtained by acetylating norlobaridone. This presumably could arise by the cleavage of the lactol ring followed by intramolecular cyclizatioo with the concomitant formation of the depsidone ring.

Thermally induced chemical artifacts in lichens have been known to occur[3]. As norlobaridone is also a major constituent of this lichen, the authenticity of norlobariol could be suspect. However, it is unlikely that norlobariol was produced from norlobaridone under the experimental conditions employed in this work. Cold extraction of the lichen with acetone over a short period yielded norlobariol. Norlobaridone under these conditions remained unchanged. It is therefore concluded that norlobariol is a natural metabolite of this lichen.

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2 G.E. Gream and N.V. Riggs, Aust. J. Chem. *13*, 285 (1960).

3 C.F. Culberson, W.L. Culberson and A. Johnson, Phytochemistry *16*, 127 (1977).

New bibenzyls of the liverwort, *Radula variabilis*

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Summary. 3 new bibenzyls having a 7-membered heterocyclic ring have been isolated from the liverwort, *Radula variabilis* and their structures have been established to be **1**, **3** and **5**.

In the course of the investigation of the aromatic components of the liverwort, we have recently reported the isolation and the structures of 4 new aromatic esters containing the isoprene units, from *Trichocolea tomentella*[1]. The liverworts, *Radula* species, also contain various aromatic compounds. We now wish to describe the isolation and the structures of 3 new bibenzyls (**1**), (**3**) and (**5**) with 7-membered heterocycle from *Radula variabilis*[2].

R. variabilis, growing on rock, was collected in June 1977. Column and preparative TLC on silica gel of the methanol extract (9 g) of air-dried and ground material resulted in the isolation of 3 new bibenzyls, **1** (9.4%, total weight of the extract), **3** (1.1%) and **5** (8.8%), respectively.

Bibenzyl (**1**), $C_{19}H_{20}O_2$ (M^+280), showed the presence of the hydroxyl group (3370 cm^{-1}) and a benzene ring (1625, 1590 and 700 cm^{-1}; λ_{max} 221 and 279 nm). The presence of a phenolic hydroxyl group was confirmed by methylation to give a monomethyl ether (**2**), $C_{20}H_{22}O_2$ (M^+ 294), NMR (figure) 3.82 ppm (s, 3H).

Hydrogenation of **2** afforded a dihydroderivative, $C_{20}H_{24}O_2$ (M^+ 296), indicating the presence of a double bond. The presence of a non-substituted benzyl group was confirmed