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SPECIALIA

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Naphthoquinones in defensive secretion of an opilionid[1]

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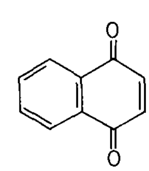
Summary. The defensive secretion of the opilionid *Phalangium opilio* contains 1,4-naphthoquinone and 6-methyl-1,4-naphthoquinone. Naphthoquinones are of rare occurrence in arthropods, having previously been reported only from certain tenebrionid beetles.

Previous studies of the defensive secretions of opilionids showed members of the suborder Laniatores to produce alkylated 1,4-benzoquinones and phenols[3-6] and members of the suborder Palpatores to produce short-chain acyclic compounds, including ketones, alcohols, and an aldehyde[3,7-10]. We here report on a species of Palpatores, *Phalangium opilio,* which is anomalous in that it produces naphthoquinones.

Phalangium opilio is a European species that has become established in parts of North America. Several hundred specimens of both sexes were collected in the vicinity of Ithaca, Tompkins County, New York, and 'milked' of secretion in the laboratory. For that purpose, small sections of capillary tubing were pressed against 1 of the 2 gland openings of each animal, thereby causing secretion from that gland to be squirted into the tube. Since the animals discharged from both glands at once, half their secretion was inevitably lost.

Gas chromatographic-mass spectrometric (GC-MS) analyses (2.4 m × 2 mm column, 2% OV-17 on Gas Chrom Q, 100–250 °C) showed the presence of 2 major components in the secretion of both sexes, in the ratio of 4–6:1. The principal component was identified as 1,4-naphthoquinone (**1**) on the basis of its characteristic mass spectrum (M^+ 158, 100%)[11]. The assignment was confirmed by co-injection with an authentic sample. It was calculated (gas chromatography; napthalene as internal standard) that a minimum of circa 0.5 µg of this quinone had been discharged per gland. The mass spectrum of the 2nd component (M^+ 172, 100%) indicated that it was closely related to 1,4-naphthoquinone but that it contained an additional CH_2 unit. Comparison of its mass spectrum with that previously reported for 2-methyl-1,4-naphthoquinone[11] ruled out that particular isomer and left 5-methyl- and 6-methyl-1,4-naphthoquinone (**2** and **3**) as possibilities. These compounds were synthesized by Diels-Alder reaction of 1,4-benzoquinone with piperylene and isoprene respectively, and subsequent oxidation. The reaction of isoprene with benzoquinone was carried out most conveniently at 35 °C in aqueous medium, for under these conditions the addition product crystallized from the reaction mixture[12]. Following oxidation of the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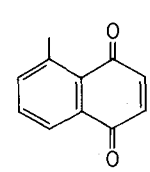
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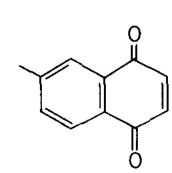
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addition products with $Na_2Cr_2O_7$[13], the quinones were identified by their melting points and nuclear magnetic resonance spectra [**2**: m.p. 106–107 °C (102–103 °C, 122.5–123 °C[14,15]); NMR ($CDCl_3$) δ 2.77 (s, 3H, CH_3), 6.92 (s, 2H, 2-, and 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].

1 Paper No. 60 of the series: Defense Mechanisms of Arthropods.

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

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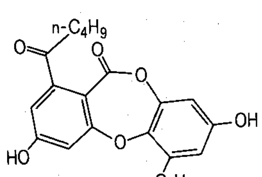
Summary. Norlobariol (I) previously described as a synthetic product derived from norlobaridone (**II**) was isolated as a new metabolite from *Xanthoparmelia scabrosa* (Tayl.) Hale.

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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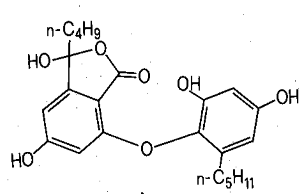
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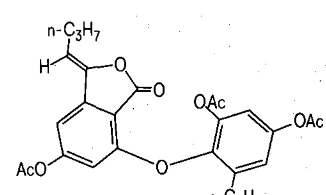
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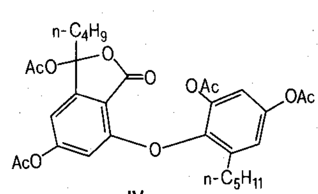
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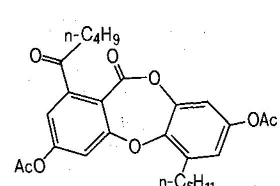
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