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BINAPHTHOQUINONES IN *LOMATIA FERRUGINEA*

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Key Word Index—*Lomatia* spp.; Proteaceae; valdivione; 2-hydroxy-3,3′-bi-1,4-naphthoquinonyl; lawsone; bi-lawsone.

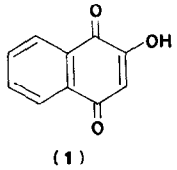
Abstract—The seeds of *Lomatia ferruginea* (Cav.) R.Br contain valdivione (2-hydroxy-3,3′-bi-1,4-naphthoquinonyl), lawsone and 3,3′-bi-lawsone present as sodium and calcium salts. No quinones were found in the seeds of *L. hirsuta* and *L. dentata*.

Hooker [1] reported that the naphthoquinone lomatiol occurred in the seeds of several Australian *Lomatia* spp. (Proteaceae) but not in the seeds of three South American spp. We recently confirmed [2] these observations with respect to the Australian seeds and found that juglone was also present in three species. We now confirm the absence of lomatiol from the Chilean spp. and report the presence of new quinones in *L. ferruginea*.

The seeds of *L. hirsuta* were grey and completely devoid of extractable colour. Some orange–brown pigment could be removed from the seeds of *L. dentata* with hot aqueous ethanol but it was not quinonoid. However, quinones were found in the seeds of *L. ferruginea* but, surprisingly, both lomatiol and juglone were absent. The red material extracted with chloroform was water-soluble although it was neither a glycoside nor an *O*-sulphate. Metal analysis (DC arc spectrography) showed that the pigments were mainly sodium (and a little calcium) salts, and after adjustment to pH 4 the free pigments could be transferred to chloroform, and separated into two components by PLC.

The main pigment, valdivione,* $C_{20}H_{10}O_5$, gave a red solution (λ_{max} 478 nm) in aqueous sodium bicarbonate which changed to pale yellow on addition of dithionite. Both the UV and IR spectra showed a strong resemblance to those of lawsone (**1**) (see Experimental) as did the NMR spectrum which comprised two multiplets at δ 8·11 and 7·75 and a singlet at δ 7·06 (Ar<u>H</u>:QH = 8:1). These facts suggested structure (**2**) for valdivione which was supported by the MS. In addition to characteristic losses of CO and ·CHO giving peaks

* The seeds were collected in Valdivia province, Chile.



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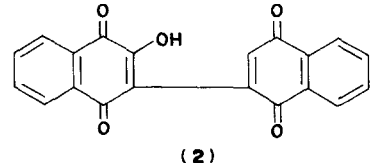

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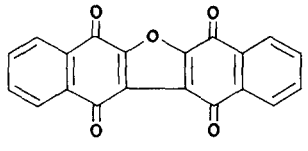

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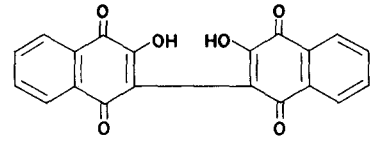

(4)

at *m/e* 300 (M), 302, 274, 246, 218, 190 and 189, and intense ions at *m/e* 105, 104, 77 and 76 expected from the individual naphthoquinone moieties [3], a significant peak at *m/e* 328 (25%, M-2) was followed by the sequence *m/e* 300, 272, 244, 216, 188 and 187, giving a "doublet" appearance to the spectrum. We attribute the peak at *m/e* 328 to the radical-ion of (**3**) as the fragmentation pattern derived from it was virtually identical with the spectrum of the diquinone (**3**) [4].

Finally structure (**2**) was confirmed by synthesis. Oxidation of 2,2'-bi-1,4-naphthoquinonyl with sodium perborate gave a small amount of the monohydroxy quinone (**2**), the major product being the dihydroxy analogue (**4**). Presumably both compounds were formed by hydrolysis of the intermediate epoxides [5].

The minor component of the pigment mixture from the *ferruginea* seeds was identical with 3,3'-bi-lawsone (**4**), and a trace of lawsone (**1**) was found in the mother liquors of (**2**).

The biogenesis of valdivione is intriguing. Lawsone (**1**) can be oxidatively dimerised to (**4**) *in vitro* [6], and as this occurs merely by exposing a solution to light [4], the bi-lawsone we found in *L. ferruginea* could be an artefact. Selective reduction of (**4**) (regarded as an enolised β-diketone) to (**2**) can be envisaged. Alternatively (**2**) could arise by phenolic coupling of a precursor [7] of (**1**) followed by selective oxidation.

EXPERIMENTAL

Spectra were run in MeOH (UV), $CHCl_3$ (IR), and $CDCl_3$ (NMR) unless otherwise stated.

Extraction of L. ferruginea *seeds.* The seeds (*ca* 30 g), after removal of the outer covering, were extracted with $CHCl_3$ (1 litre). Evaporation left a black residue (2·7 g) which was taken up in $CHCl_3$ (100 ml), filtered from black material (1 g), concentrated, and applied to PLC plates (SiO_2) which were developed with $CHCl_3$–MeOH (19:1). The red band (R_f 0·12) was eluted with MeOH. After further chromatography, and precipitation from $CHCl_3$–MeOH the hydroxyquinone salts were obtained as an amorphous red solid, dec 343–344° (20 mg) [Found: Na, 8% (±10%); Ca, 1·1% (±10–20%)], λ_{max} 232, 269, 456 nm, ν_{max} (KBr) 3410 (br), 1680, 1615, 1591, 1550 cm^{-1}. Dissolution in pH 4 buffer (10 ml) followed by extraction with $CHCl_3$ and evaporation gave an orange solid (10 mg). After removal of (**4**) (R_f 0·04) by TLC *valdivione* (**2**) (R_f 0·25) crystallized from C_6H_6–hexane as orange needles, mp 185–186° (dec) (5 mg) (Found: M^+, 330·0528. $C_{20}H_{10}O_5$ requires M^+, 330·0528), λ_{max} 217, 268, 335 (sh) nm (log ε 4·30, 4·47, 3·64), λ_{max} (MeOH–HO^-) 268, 478 nm (log ε 4·47, 3·54) [*cf.* lawsone (**1**) 248, 274, 334 nm, λ_{max} (MeOH–HO^-) 232, 271, 454 nm], ν_{max} 3390, 1670, 1658, 1600 cm^{-1} [*cf* lawsone (**1**) 3410, 1680 (sh), 1665, 1602 cm^{-1}], δ 8·11 (4H, *m*, ArH), 7·75 (4H, *m*, ArH), 7·06 (1H, *s*, QH) (OH not observed) [*cf* lawsone (**1**) δ 8·11 (2H, *m*), 7·74 (2H, *m*), 7·32 (1H, *bs*, OH), 6·35 (1H, *s*, QH)], *m/e* (%) 331 (14), 330 (79), 328 (22), 314 (4·5), 302 (1·5), 300 (14), 290 (3·5), 288 (3·5), 274 (5), 272 (5·5), 246 (9), 244 (2·5), 218 (5), 216 (4·5), 200 (5·5), 190 (4·5), 189 (20), 188 (11), 187 (11), 185 (5), 174 (5·5), 155 (5·5), 149 (10), 143 (5·5), 141 (5·5), 105 (56), 104 (50), 77 (63), 76 (100).

The mother liquor yielded a trace of lawsone (**1**) identical (TLC, MS) with authentic material. Working up the second red band (R_f 0·04), as above, afforded bi-lawsone (**4**) (1 mg) identical (TLC, MS) with an authentic sample.

Synthesis of valdivione. To a stirred soln of 2,2'-bi-1,4-naphthoquinonyl (2 g) in dioxan (900 ml) was added sodium perborate (2 g) in H_2O (200 ml) during 15 min. The soln became deep red. After a further 15 min it was acidified (HCl) to pH 3 and mixed with brine (500 ml). The organic layer was separated and the aq phase was extracted with $CHCl_3$. The crude product from the combined organic layers was separated by chromatography (SiO_2) in $CHCl_3$ into starting material (0·7 g), valdivione (100 mg, 8%) and bi-lawsone, mp 280–281° (400 mg, 32%). Valdivione was further purified by TLC in $CHCl_3$–MeOH (19:1), and crystallized from C_6H_6–hexane as orange needles, mp 192–193° (Found: C, 73·0; H, 3·4%. $C_{20}H_{10}O_5$ requires C, 72·7; H, 3·0%) identical (MMP, TLC, UV, IR, MS) with the natural material. The lower MP of the natural compound may be attributable to the presence of a small amount of (**1**) observed in the MS (*m/e* 174, mass measured for $C_{10}H_6O_3$); (**1**) has the same R_f as (**2**).

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REFERENCES

1. Hooker, S. C. (1936) *J. Am. Chem. Soc.* **58**, 1181; Gibbs, R. D. (1965) *Lloydia* **28**, 279.
2. Moir, M. and Thomson, R. H. (1973) *Phytochemistry* **12**, 1351.
3. Bowie, J. H., Cameron, D. W. and Williams, D. H. (1965) *J. Am. Chem. Soc.* **87**, 5094; Moore, R. E., Brennan, M. R. and Todd, J. S. (1972) *Org. Mass Spectrom* **6**, 603.
4. Hooker, S. C. (1936) *J. Am. Chem. Soc.* **58**, 1212.
5. Rashid, A. and Read, G. (1967) *J. Chem. Soc.* (*C*) 1323.
6. Chandrasenan, K. and Thomson, R. H. (1971) *Tetrahedron* **27**, 2529.
7. Baldwin, R. M., Snyder, C. D. and Rapoport, H. (1974) *Biochemistry* **13**, 1523.