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NAPHTHAQUINONES IN *LOMATIA* SPECIES

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Key Word Index—*Lomatia* spp.; Proteaceae; lomatiol; juglone; β-hydrojuglone; naphthazarin; flavonol 3-methyl ethers.

Abstract—Lomatiol, juglone, β-hydrojuglone and naphthazarin have been found distributed in various parts of six *Lomatia* spp. Three others contained no quinonoid pigments but the leaves of *L. dentata* yielded kaempferol-3-methyl ether and quercetin-3-methyl ether.

ACCORDING to Hooker[1] the naphthaquinone lomatiol (I) occurs in the seeds of five Australian *Lomatia* (*L. illicifolia*, *L. longifolia*, *L. polymorpha*, *L. silaifolia* and *L. tinctoria*) (Proteaceae) but it was not found in the seeds of three Chilean spp. (*L. dentata*, *L. ferruginea* and *L. obliqua*). Surprisingly, no other pigments were observed but subsequently crude colour tests[2] suggested that other quinones might be present in the leaves and bark of both Australian and South American spp. We have now examined material from nine *Lomatia* spp. and the results are shown in Table 1.

TABLE 1. DISTRIBUTION OF NAPHTHAQUINONES IN *Lomatia* SPP.

Species	Lomatiol	Juglone	Naphthazarin	Species	Lomatiol	Juglone	Naphthazarin
L. arborescens				*L. longifolia*			
Seeds	+	+	−	Leaves	−	+*	−
Wood	−	+	−	Wood, bark	−	+	−
L. dentata				*L. obliqua*			
Leaves	−	−	−	Leaves	−	+†	−
Wood, bark	−	−	−	Wood, bark	−	+	+
L. ferruginea				*L. silaifolia*			
Leaves	−	−	−	Leaves	−	−	−
L. fraxinifolia				Seeds	+	+	−
Leaves	−	+	−	Wood	−	−	−
Bark	−	+	−	*L. tinctoria*			
L. hirsuta				Seeds	+	+†	−
Leaves	−	−	−	Wood, bark	−	+	−

* Identified by TLC only.
† β-Hydrojuglone also present.

We confirm the presence of lomatiol in the seeds of *L. silaifolia* and *L. tinctoria*, and found it also in the seeds of the Australian *L. arborescens*. (No other seeds were available and lomatiol was not detected elsewhere.) The seeds of these species also contained juglone

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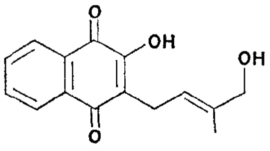
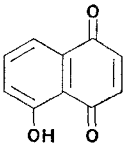
[1] HOOKER, S. C. (1936) *J. Am. Chem. Soc.* **58**, 1181.
[2] GIBBS, R. D. (1965) *Lloydia* **28**, 279.

(II) which was present in the leaves, wood and bark of several other species, thus vindicating Gibbs' 'Juglone Test A' reactions.[2] TLC of the petrol extracts from the seeds of *L. tinctoria* also revealed a colourless, UV-fluorescent band, which turned orange on exposure to air. It was isolated as a greenish yellow solid and proved to be β-hydrojuglone (III). A trace amount was also present in the leaves of *L. obliqua*. A third naphthaquinone, naphthazarin (IV), was found in the wood and bark of *L. obliqua*. No quinones were detected in our samples of *L. dentata*, *L. ferruginea* (cf. Gibbs[2]) and *L. hirsuta* material but the methanol extract from the leaves of *L. dentata* yielded the flavonols kaempferol-3-methyl ether and quercetin-3-methyl ether.


(I)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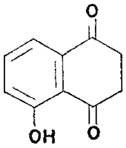
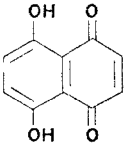

(III)


(IV)

Naphthazarin (IV) and β-hydrojuglone (III) are new natural products, and juglone has not been found previously outside the Juglandaceae.[3] In this family it occurs mainly in reduced glycosidic form [1,4,5-trihydroxynaphthalene (α-hydrojuglone) 4-β-D-glucoside in *Juglans regia*[4]]; β-hydrojuglone has also been reported[5] but was an artefact of isolation. 7-Methyl-β-hydrojuglone has been found[6] in *D. ebenum* (Ebenaceae) along with 7-methyljuglone.

Lomatiol is a prenylated lawsone (2-hydroxy-1,4-naphthaquinone) and the co-existence of lomatiol and juglone in certain *Lomatia* is consistent with recent studies[7] on the biogenesis of lawsone and juglone. The naphthaquinone nucleus of both of these appears to derive from shikimic acid and glutamate by way of *o*-succinoylbenzoic acid, and presumably lomatiol is formed in the same way, prenylation occurring at a late stage.

EXPERIMENTAL

Known compounds were identified by direct comparison (TLC, UV, IR) with authentic specimens (except for quercetin-3-methyl ether). TLC separations were effected on silica gel/3% oxalic acid plates in $CHCl_3$ unless otherwise stated.

Extraction of seeds. L. tinctoria seeds (*ca.* 4 g) were extracted (Soxhlet) with petroleum (200 ml) and $CHCl_3$ (200 ml). The petroleum solution deposited lomatiol, m.p. 126–7° (lit.[3] 127°) (3 mg). The filtrate and $CHCl_3$ extract were combined and concentrated. TLC gave three bands. Band 1 (R_f 0·1) was lomatiol (2 mg). Band 2 (R_f 0·65) yielded a greenish yellow solid (3 mg) giving an intensely yellow UV-fluorescent solution. It crystallised from $CHCl_3$ as needles, m.p. 96–7° (evacuated Pyrex capillary) (lit.[8] 96–7°) identical with β-hydrojuglone. After leaving on the plate overnight, in air, this band turned orange and gave orange needles of juglone on elution. Band 3 (R_f 0·7) afforded juglone (5 mg) after further purification on a column of acid-washed silica gel in $CHCl_3$. Similarly seeds of *L. arborescens* and *L. silaifolia* (each 1 5 g) gave lomatiol (5 mg) and juglone (2 mg); β-hydrojuglone was not detected.

[3] Thomson, R. H. (1971) *Naturally Occurring Quinones*, 2nd Edn, Academic Press, London.

[4] Hayes, N. F. and Thomson, R. H. (1955) *J. Chem. Soc.* 904; Gupta, S. R., Ravindranath, B. and Seshadri, T. R. (1972) *Phytochemistry* **11**, 2634.

[5] Mylius, F. (1884) *Chem. Ber.* **17**, 2411; *idem.* (1885) **18**, 2567.

[6] Cooke, R. G. and Dowd, H. (1952) *Australian J. Sci. Res.* **5A**, 760.

[7] Zenk, M. H. and Leistner, E. (1967) *Z. Naturforsch.* **22b**, 460; Campbell, I. M. (1969) *Tetrahedron Letters* 4777; Leduc, M. M., Dansette, P. M. and Azerad, R. G. (1970) *European J. Biochem.* **15**, 428; Dansette, P. and Azerad, R. (1970) *Biochem. Biophys. Res. Commun.* **40**, 1090.

[8] Thomson, R. H. (1950) *J. Chem. Soc.* 1737.

Extraction of bark. Chopped bark (560 g) of *L. obliqua* was successively extracted with petroleum (8 l.) and $CHCl_3$ (8 l.). The latter yielded 2·5 g of material, 25% of which was separated by PLC on silica gel in hexane–butanone (5:1) giving two major coloured bands. Band 1 (orange, R_f 0·45) yielded brown crystals which were sublimed at 80°/0·1 mm to give juglone, m.p. 163–4° (Pyrex) (lit.[3] 164–5°) (38 mg). Band 2 (violet, R_f 0·32) gave naphthazarin (5 mg) as deep red needles, m.p. 272–4° (evacuated Pyrex capillary) (petrol.–dichloromethane), τ ($CDCl_3$) 2·40 (*s*, 2H, OH) and 2·85 (*s*, 4H, ArH and QH). Similarly the bark of *L. tinctoria* (15 g), *L. arborescens* (20 g), *L. longifolia* (4 g) and *L. fraxinifolia* (2 g) gave juglone (< 1 mg in each case).

Extraction of wood. Trace amounts of juglone were obtained from $CHCl_3$ extracts (see Table).

Extraction of leaves. Finely chopped leaves of *L. obliqua* (15 g) were extracted with petroleum (300 ml) and $CHCl_3$ (300 ml). The latter, after concentration and TLC yielded juglone (5 mg) and β-hydrojuglone (< 1 mg). The leaves of *L. fraxinifolia* (5 g) and *L. longifolia* (2 g) gave juglone only (10 mg and a trace, respectively). Leaves (5 g) of *L. dentata* were extracted with $CHCl_3$ (50 ml) and MeOH (50 ml). The former yielded only chlorophylls but the latter extract gave two pigments separated by TLC on silica gel in $CHCl_3$. Band 1 (R_f 0·3) yielded kaempferol-3-methyl ether (2 mg), yellow needles, m.p. 279–80° (aq. MeOH) (lit.[9] 276°). Band 2 (R_f 0·25) gave quercetin-3-methyl ether (5 mg), yellow needles, m.p. 273–5° (aq. MeOH) (lit.[9] 275°), λ_{max} (MeOH) 257, 294, 358 nm (MeOH–MeONa) 407 nm (MeOH–$AlCl_3$) 443 nm.

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[9] PACHECO, H. and GROUILLER, A. (1965) *Bull. Soc. Chim. Fr.* 779.