Tanaka, O. (1979) *Tetrahedron* **35**, 1427.
16. Mahato, S. B., Sahu, N. P., Ganguly, A. N., Kasai, R. and Tanaka, O. (1980) *Phytochemistry* **19**, 2017.
17. Eggert, H. and Djerassi, C. (1975) *Tetrahedron Letters* **42**, 3635.
18. Klyne, W. (1950) *Biochem. J.* **47**, 41.
19. Misra, S. B. and Mohan Rao, V. K. (1960) *J. Sci. Ind. Res.* **19**, 173.
20. Hostettmann, K., Kizu, H. and Tomimori, T. (1982) *Planta Med.* **44**, 34.

Phytochemistry, Vol. 25, No. 6, pp. 1494–1495, 1986.
Printed in Great Britain.
0031-9422/86 $3.00 + 0.00

NAPHTHOQUINONES FROM JUGLANDACEAE

Kiyoichi Hirakawa, Eriko Ogiue, Jiro Motoyoshiya and Masao Yajima

Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386, Japan

(*Received* 16 *September* 1985)

Key Word Index—*Pterocarya*; *Juglans*; Juglandaceae; juglone; 3,3′-bijuglone; cyclotrijuglone.

Abstract—The oligomeric juglones isolated from the barks of Juglandaceae plants, *Pterocarya* and *Juglans*, were shown to be 3,3′-bijuglone (8,8′-dihydroxy[2,2′-binaphthalene]-1,1′,4,4′-tetrone and unsymmetrical cyclotrijuglone (1,7,16-trihydroxy-5,6,11,12,17,18-trinaphthalenehexone).

INTRODUCTION

It is well known that juglone (5-hydroxy-1,4-naphthoquinone) and hydrojuglone glucoside (4,8-dihydroxy-1-naphthalenyl-β-D-glucopyranoside) occur in different parts of Juglandaceae [1]. Other monomeric naphthoquinones have also been found (e.g. 1,4-naphthoquinone [2, 3] and 5,8-dihydroxy-1,4-naphthoquinone [4] from *Juglans* species). The natural co-occurrence of a monomeric quinone with its oligomers (dimer, trimer and tetramer) has been widely studied, e.g. 7-methyljuglone (ramentacenone) and its oligomers in Ebenaceae and 2-methyljuglone (plumbagin) and its oligomers in Droseraceae [1]. However, the oligomers from the quinones which occur among Juglandaceae plants have received little attention. Juglone oligomers, 3,3′-bijuglone (**1**) [5] and symmetrical cyclotrijuglone (**2**) [6], have been reported to occur in root-bark of *J. regia* in one instance only. The present paper is concerned with the isolation and structure elucidation of juglone oligomers from *P. rhoifolia* Sieboldiana et Zucc. (wingnut, Japanese name Sawagurumi) and *J. mandshurica* Maxim. var. Sieboldiana Makino (walnut, Japanese name Onigurumi).

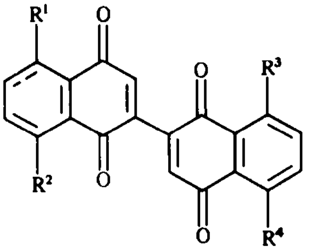
RESULTS AND DISCUSSION

The chloroform extracts of the fresh root-bark of *P. rhoifolia* was chromatographed on silica gel (benzene as eluant) to give in addition to juglone two polar light yellow compounds. The less polar of the two polar compounds was identified as bijuglone (**1**) by comparison with an authentic sample prepared by addition of juglone and 1,4,5-trihydroxynaphthalene [7]. The ^{1}H NMR spectrum ($CDCl_3$) of isolated **1** revealed two singlets of H-3 and H-3′ (δ7.04) and 8- and 8′-OH (δ11.75). Bijuglone (**1**) was distinguished from its isomers, 2,2′-bijuglone (**3**) and 2,3′-bijuglone (**4**), by ^{1}H NMR spectroscopy [8, 9]*. It gave a reddish violet colour with aqueous alkali and underwent reversible reduction with sodium dithionite like many other hydroxynaphthoquinones.

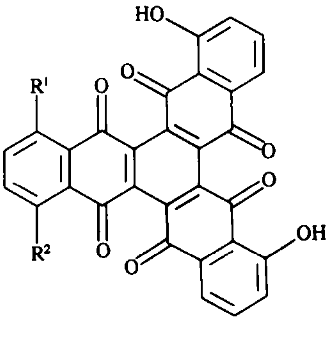
The second polar compound was unsymmetrical cyclotrijuglone (**5**), having hydroxyl groups at the unsymmetrical position. The structure followed from the ^{1}H NMR spectral data (1- and 16-OH singlet and 7-OH singlet at δ11.20 and 11.27, respectively, in $CDCl_3$). The structure of cyclotrijuglone from *J. regia* had previously been assigned as symmetrical **2** rather than unsymmetrical **5** [6]. More recently, synthetic cyclotrijuglone has been obtained from the addition of juglone to 1,4,5-trihydroxynaphthalene followed by treatment with chloranil. Its structure was assigned as **5** on the grounds that the ^{1}H NMR spectrum ($CDCl_3$) of its triacetate showed two singlet signals at δ2.51 (3H, OAc) and 2.48 (6H, 2OAc) [7]. The ^{1}H NMR spectrum ($CDCl_3$) of cyclotrijuglone from

---

*The chemical shifts ($CDCl_3$/TMS = 0) for vinyl and hydroxyl protons of **3** and **4**, prepared independently by the method of Laatsch [8, 9], are as follows. Compound **3**: δ7.05 (2H, *s*, H-3 and H-3′), 11.86 (2H, *s*, 5- and 5′-OH); **4**: δ7.02 (1H, *s*, H-3′), 7.06 (1H, *s*, H-3), 11.73 (1H, *s*, 8′-OH), 11.85 (1H, *s*, 5-OH).



1 $R^1 = R^4 = H$, $R^2 = R^3 = OH$
3 $R^1 = R^4 = OH$, $R^2 = R^3 = H$
4 $R^1 = R^3 = OH$, $R^2 = R^4 = H$



2 $R^1 = H$, $R^2 = OH$
5 $R^1 = OH$, $R^2 = H$

P. rhoifolia was identical with that of a synthetic sample. Isolated **5** gave a pinkish violet colour with aq. alkali and reversible reduction with sodium dithionite. TLC analysis of chloroform extracts of stem-barks and green parts in *P. rhoifolia* showed the presence of juglone, **2** and **5**, in much smaller quantities than those in root-barks. In all runs, juglone was the principal component (see Experimental).

A similar isolation from root- and stem-barks of *J. mandshurica* gave comparable results, and the contents of naphthoquinones were much higher than those from *P. rhoifolia* (see Experimental). The differences in contents of free naphthoquinones between *Pterocarya* and *Juglans* may vary with different seasons and surroundings [10]. This is the first report of co-occurrence of juglone, 3,3′-bijuglone and unsym-cyclotrijuglone in *Pterocarya*. This co-occurrence may be found widely among Juglandaceae plants.

EXPERIMENTAL

Plant materials were taken from 15–20-yr-old wingnut and walnut plants (grown from seeds) in early August.

Isolation of naphthoquinones. The $CHCl_3$ extracts (1 L) of fresh bark (100 g) of *Pterocarya* (or *Juglans*) were washed repeatedly with H_2O, dried and concd. The residue was chromatographed on silica gel with C_6H_6. The second eluate contained juglone as light yellow needles, identical with an authentic specimen. The fourth fraction consisted of 3,3′-bijuglone (**1**) as light yellow microcrystals (from $CHCl_3$), mp 275–278° (decomp) (lit. 285° [8]). R_f 0.30 ($CHCl_3$: Merck, silica gel $60F_{254}$, pre-coated plastic sheet, 0.2 mm); IR ν_{max}^{KBr} cm^{-1}: 1660, 1625 (CO); ^1H NMR (90 MHz, $CDCl_3$): δ7.04 (2H, *s*, H-3 and H-3′), 7.26–7.42 (2H, *m*, H-7 and H-7′), 7.62–7.76 (4H, *m*, H-5, H-6, H-5′ and H-6′), 11.75 (2H, *s*, 8- and 8′-OH); MS (75 eV) *m/z* (rel. int.): 346 $[M]^+$ (100), 329 (24), 318 (11), 290 (18), 289 (20), 262 (20), 234 (11), 205 (10), 120 (18), 92 (35), 64 (16), 63 (17). The fifth gave cyclotrijuglone (**5**) as light yellow microcrystals (from $CHCl_3$), mp 375–377° (decomp) (lit. > 360° [7]). R_f 0.26 ($CHCl_3$); IR ν_{max}^{KBr} cm^{-1}: 1692, 1680, 1640 (CO); ^1H NMR ($CDCl_3$): δ7.25–7.45 (3H, *m*, H-2, H-8 and H-15), 7.60–7.80 (6H, *m*, H-3, H-4, H-9, H-10, H-13 and H-14), 11.20 (2H, *s*, 1- and 16-OH), 11.27 (1H, *s*, 7-OH); MS (75 eV) *m/z* (rel. int.): 516 $[M]^+$ (100), 488 (29), 460 (17), 432 (16), 404 (16), 376 (10), 263 (11), 258 (12), 92 (105), 63 (11). The yields of isolation products (mg/100 g fr. wt) were as follows: *Pterocarya* root-bark: juglone, 33, 1, 6, 5, 2; *Pterocarya* stem-bark: 24, 5, 1; *Juglans* root-bark: 330, 52, 30; *Juglans* stem-bark: 99, 21, 10.

REFERENCES

1. Thomson, R. H. (1971) in *Naturally Occurring Quinones*, Chap. 4. Academic Press, London.
2. Mueller, W.-U. and Leistner, E. (1976) *Phytochemistry* **15**, 407.
3. Mueller, W.-U. and Leistner, E. (1978) *Phytochemistry* **17**, 1739.
4. Ohta, A., Sivalingam, P. M., Lin, S. and Ikekawa, N. (1973) *Toxicon* **11**, 235.
5. Pardhasaradhi, M. and Babu, M. H. (1978) *Phytochemistry* **17**, 2042.
6. Sindhu, G. S., Pardhasaradhi, M. and Babu, M. H. (1975) *Indian J. Chem.* **13**, 749.
7. Brockmann, H. and Laatsch, H. (1983) *Justus Liebigs Ann. Chem.* 433.
8. Laatsch, H. (1980) *Justus Liebigs Ann. Chem.* 1321.
9. Laatsch, H. (1983) *Justus Liebigs Ann. Chem.* 1020.
10. Lee, K. C. and Campbell, R. W. (1968) *Hort. Science* **4**, 297.