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GUAIANE SESQUITERPENES FROM *MAGNOLIA WATSONII*

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Key Word Index—*Magnolia watsonii*, Magnoliaceae, sesquiterpenes, dehydrocostuslactone, watsonol A, watsonol B, 15-acetoxycostunolide, neolignans, obovatol, aporphine alkaloids

Abstract—The leaves and the trunk barks of *Magnolia watsonii* afforded two biosynthetic intermediates of dehydrocostuslactone (watsonol A and watsonol B) along with the neolignans, magnolol, hōnokiol and obovatol, and the aporphine alkaloids, liriodenine and asimilobine

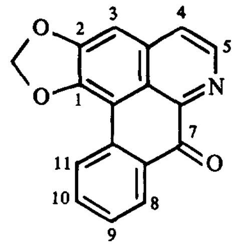
In a recent chemotaxonomical investigation of the sesquiterpenes and the neolignans of magnoliaceous plants [1–6], it was found that the chloroform extracts of *Magnolia watsonii* Hook. fil contained two biosynthetic intermediates of dehydrocostuslactone (**11**), named watsonol A (**12**) and watsonol B (**13**). We now wish to report on the characterization of these new guaiane sesquiterpenes

The chloroform extracts of the fresh leaves and the trunk bark of *M watsonii* afforded three guaiane sesquiterpenes, the major one of which was identified as dehydrocostuslactone (**11**) [7, 8] The second sesquiterpene, watsonol A, mp 65–67°, $C_{15}H_{22}O_2$ (M^+ 234), was obtained as a crystalline substance Its IR spectrum ($CHCl_3$) showed bands assignable to a hydroxyl group (3430 cm^{-1}), and a double bond (1640 cm^{-1}) The ^1H NMR spectrum ($CDCl_3$) resembled that of dehydrocostuslactone (**11**), except for the presence of signals due to a hydroxymethylene group (δ4 06) in place of the γ-butyrolactone function of **11** Acetylation of watsonol A with acetic anhydride and pyridine afforded a diacetate, which showed two acetoxyl methyl signals at δ1 87 and 2 06 in its ^1H NMR spectrum In addition, the ^1H NMR spectrum exhibited signals typical of three terminal methylene double bonds (1H, *d*, $J = 2$ Hz, δ4 73, 1H, *s* (*br*), δ4 82, 1H, *s*, δ4 94, 1H, *s*, δ5 07, 2H, *s*, δ5 11) at C-15, C-14 and C-13, and a 1H as a triplet at δ3 27 ($J = 9$ Hz) for the proton attached to the carbon bearing the hydroxyl group at C-6 The latter signal shows the *trans*-diaxial disposition of the protons at C-5 (α), C-6 (β) and C-7 (α), as in dehydrocostuslactone (**11**)

On Jones oxidation of watsonol A, the oxidation product was obtained The structure of this compound was in agreement with dehydrocostulactone (**11**) (IR, MS and ^1H NMR) Therefore, the stereostructure of watsonol A is confirmed to be **12**

The third guaiane sesquiterpene, watsonol B, $C_{17}H_{24}O_3$ (M^+ 276), was obtained as an oil Its IR spectrum contained bands assignable to a hydroxyl group (3530 cm^{-1}), an acetoxyl group (1725 cm^{-1}), and a double bond (1640 cm^{-1}) The ^1H NMR spectrum was superimposable on that of watsonol A (**12**), except for the presence of a signal due to an acetoxyl methyl group

Watsonol B was acetylated with acetic anhydride and pyridine to give an acetate, which was identical with a diacetate of watsonol A Thus, the structure of watsonol B is elucidated as **13** Besides the three guaiane sesquiterpenes, the germacranolide sesquiterpenes, costunolide (**9**) and 15-acetoxycostunolide (**10**) [9], and the eudesman sesquiterpenes, α-eudesmol (**6**), β-eudesmol (**7**) and cryptomeridiol (**8**) [10] were isolated and characterized from the chloroform extracts of the fresh leaves and the trunk



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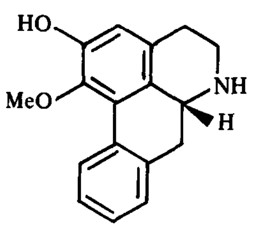

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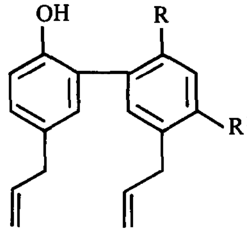
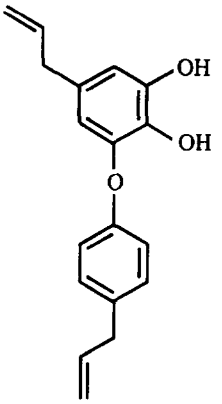


3 R = OH, R^1 = H
4 R = H, R^1 = OH



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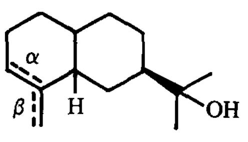
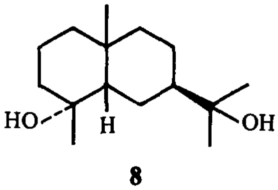


6 α–
7 β–



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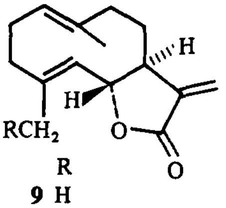
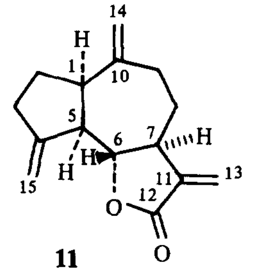


R
9 H
10 OAc



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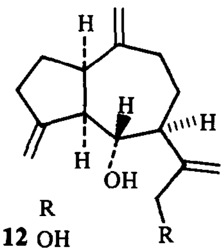

R
12 OH
13 OAc

bark of this plant Furthermore, three phenolic neolignans, magnolol (**3**), honokiol (**4**) [10] and obovatol (**5**) [3], and two aporphine alkaloids, liriodenine (**1**) and asimilobine (**2**) [11] were isolated from the trunk bark of this plant as well as from *M obovata* Thunb

EXPERIMENTAL

Mps uncorr, ^{1}H NMR (100 MHz) and ^{13}C NMR (25 MHz) $CDCl_3$, int standard TMS, MS (70 eV) direct insertion, IR $CHCl_3$, UV and CD MeOH CC silica gel 60 (70–230 mesh), TLC silica gel F-254 (0 25 mm) Spots were detected on TLC in UV light (254 nm) after spraying with 10% H_2SO_4 and then heating at 100°

Extraction and separation of compounds The MeOH extracts of fresh leaves (1 5 kg) and trunk bark (3 5 kg) of *M watsonii* collected in Sept 1982 in the Yawase district, Inazawa, Aichi prefecture, were separated into *n*-hexane and $CHCl_3$-soluble fractions respectively The basic fraction from the $CHCl_3$ extract (trunk bark) (4 8 g) was chromatographed over Brockmann Al_2O_3 (Standard II-III) ($CHCl_3$) to give liriodenine (**1**, 38 mg) and asimilobine (**2**, 54 mg). The neutral fraction (leaf) (15 g) was chromatographed over a column of silica gel (120 g) using C_6H_6 as eluent to afford dehydrocostuslactone (**11**, 40 mg), watsonol B (**13**, 107 mg), watsonol A (**12**, 10 mg) and 15-acetoxycostunolide (**10**, 88 mg) The neutral fraction (trunk bark) (62 g) was chromatographed over a column of silica gel (500 g) using C_6H_6 with gradually increasing proportions of EtOAc as eluent The first fraction (C_6H_6) gave costunolide (**9**, 44 mg), dehydrocostuslactone (**11**, 125 mg), 15-acetoxycostunolide (**10**, 78 mg), α-eudesmol (**6**, 8 mg), β-eudesmol (**7**, 10 mg), cryptomeridiol (**8**, 27 mg), obovatol (**5**, 1 5 g), magnolol (**3**, 187 mg) and hōnokiol (**4**, 300 mg) The second fraction (C_6H_6–EtOAc, 5 1) gave watsonol B (**13**, 107 mg) and watsonol A (**12**, 89 mg)

Dehydrocostuslactone (**11**) Colourless oil IR $\nu_{\max}^{CHCl_3}$ cm^{-1} 1755, 1640, 1000, UV $\lambda_{\max}^{MeOH}$ nm (ε) 206 (8168), MS *m/z* 230 $[M]^+$ ($C_{15}H_{18}O_2$), CD (*c* 0 013, MeOH) $[\theta]_{290}$ 0, $[\theta]_{265}$ −708, $[\theta]_{221}$ −14154, $[\theta]_{211}$ 0, ^{1}H NMR δ3 94 (1H, *t*, *J* = 10 Hz, H-6), 4 82 (1H, *s*, H-14), 4 88 (1H, *s*, H-14), 5 04 (1H, *d*, *J* = 2 Hz, H-15), 5 25 (1H, *d*, *J* = 2 Hz, H-15), 5 48 (1H, *d*, *J* = 3 Hz, H-13), 6 29 (1H, *d*, *J* = 3 Hz, H-13), ^{13}C NMR δ30 3, 30 9 (each *t*, C-2 or C-3), 32 6, 36 3 (each *t*, C-8 or C-9), 45 1, 52 0 (each *d*, C-1 or C-5), 47 6 (*d*, C-7), 85 2 (*d*, C-6), 109 5, 112 6 (each *t*, C-14 or C-15), 120 0 (*t*, C-13), 139 8 (*s*, C-11), 149 2, 151 3 (each *s*, C-4 or C-10), 170 1 (*s*, C-12)

Watsonol B (**13**) Colourless oil IR $\nu_{\max}^{CHCl_3}$ cm^{-1} 3530; 1725, 1640, MS *m/z* 276 $[M]^+$ ($C_{17}H_{24}O_3$), 258, 216, 198, ^{1}H NMR δ2 08 (3H, *s*, OCOMe), 3 18 (1H, *t*, *J* = 9 Hz, H-6), 4 58 (2H, *s*, H-12), 4 69 (1H, *d*, *J* = 2 Hz, H-15), 4 78 (1H, *s* (*br*), H-15), 4 92 (1H, *s*, H-14), 5 03 (1H, *s*, H-14), 5 06 (2H, *s*, H-13), ^{13}C NMR δ21 0 (*q*, $OCO\underline{Me}$), 28 8, 30 7 (each *t*, C-8 or C-9), 35 3, 35 9 (each *t*, C-2 or C-3), 47 4 (*d*, C-1), 53 6, 55 4 (each *d*, C-5 or C-7), 65 9 (*t*, C-12), 68 8 (*d*, C-6), 110 6, 111 2, 111 9 (each *t*, C-13 or C-14 or C-15), 147 5 (*s*, C-11), 152 2, 153 0 (each *s*, C-4 or C-10), 170 7 (*s*, $O\underline{C}OMe$)

Watsonol A (**12**) Colourless needles, mp 65–67° IR $\nu_{\max}^{CHCl_3}$ cm^{-1} 3600, 3430, 1640, MS *m/z* 234 $[M]^+$ ($C_{15}H_{22}O_2$), 216, 198, ^{1}H NMR δ3 27 (1H, *t*, *J* = 9 Hz, H-6), 4 06 (2H, *s*, H-12), 4 73 (1H, *d*, *J* = 2 Hz, H-15), 4 82 (1H, *s* (*br*), H-15), 4 94 (1H, *s*, H-14), 5 07 (1H, *s*, H-14), 5 11 (2H, *s*, H-13)

Jones oxidation of watsonol A To a soln of **12** (5 mg) in Me_2CO (2 ml), Jones reagent (8 N CrO_3 soln) (15 mg) was added at 0° After 1 min, H_2O was added and the mixture extracted with $CHCl_3$ Evaporation of $CHCl_3$ gave a gum, which was chromatographed on Al_2O_3 (C_6H_6) to give pure dehydrocostuslactone (**11**, 2 mg)

Diacetate of watsonol A Colourless oil IR $\nu_{\max}^{CHCl_3}$ cm^{-1} 1725, 1640, 900, MS *m/z* 318 $[M]^+$ ($C_{19}H_{26}O_4$), 258, 198, ^{1}H NMR δ1 87 (3H, *s*, OAc-6), 2 06 (3H, *s*, OAc-12), 4 47 (2H, *s*, H-12), 4 72 (1H, *t*, *J* = 9 Hz, H-6), 4 76–5 04 (6H, *m*, H-13, H-14, H-15)

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