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ISOFLAVONES FROM *DIPTERYX ODORATA*

TERUO HAYASHI and RONALD H. THOMSON

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, Scotland

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Key Word Index—*Dipteryx odorata*; Leguminosae; isoflavones; retusin; retusin 8-methyl ether; 3'-hydroxyretusin 8-methyl ether; 7,3'-dihydroxy-6,4'-dimethoxyisoflavone; 7,8-dihydroxy-6,4'-dimethoxyisoflavone.

Abstract—Five isoflavones have been isolated from the heartwood of *Dipteryx odorata*: retusin, retusin 8-methyl ether, 3'-hydroxyretusin 8-methyl ether, odoratin (7,3'-dihydroxy-6,4'-dimethoxyisoflavone) and dipteryxin (7,8-dihydroxy-6,4'-dimethoxyisoflavone).

INTRODUCTION

ACCORDING to an old report,[1] a wood called "Tonquin" yields a bright red sawdust, and when a workman attempted to remove the dust from his hair by dipping his head in a bucket of water, his hair turned a bright grass-green colour! Intrigued by this striking colour change we attempted to obtain some "Tonquin" wood but nothing is recorded[1] beyond the name and the fact that it "was received from an East Indian Island". It seemed possible that "Tonquin" was the wood from the tonquin or tonka bean tree (*Dipteryx odorata* = *Coumarouna odorata*), the seeds of which are the original source of coumarin. However, the heartwood of *D. odorata* does not provide red sawdust nor does it turn green, and we report here on the isoflavone constituents.

RESULTS AND DISCUSSION

After defatting with petrol the heartwood was extracted (Soxhlet) with chloroform from which five isoflavones were isolated. Two of these were insoluble in cold chloroform, and were readily separated from the others.

Compound 1, the major component, $C_{17}H_{14}O_5$, ν_{CO} 1640 cm^{-1}, contained a hydroxyl and two methoxyl groups, and showed a characteristic isoflavonoid 2–H singlet at δ 7·95 in the NMR spectrum. The aromatic proton signals comprised an AB quartet centred at δ 7·04 and 7·96 clearly attributable to H-6 and H-5, and another (4H) at δ 6·96 and 7·48 from ring B which must be substituted at the 4'-position. As the UV maxima undergo bathochromic shifts on addition of sodium acetate the hydroxyl group must be located at C-7 which leads to structure (**1**; R=H, R'=Me) (retusin 8-methyl ether)[2] for compound 1. This was confirmed by direct comparison of the acetate with an authentic sample.[2]

Compound 2, $C_{16}H_{12}O_5$, one of the components insoluble in cold chloroform showed spectral characteristics very similar to those of retusin 8-methyl ether but possessed only one methoxyl group. As the UV spectrum gave a bathochromic shift with sodium acetate, and the compound formed a complex with sodium molybdate,[3] it appeared to be retusin

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[1] THOMPSON, W. G. (1914) *The Occupational Diseases*, D. Appleton, London.

[2] JURD L., STEVENS K., and MANNERS, G. (1972) *Phytochemistry* **11**, 2535.

[3] PRIDHAM, J. B. (1959) *J. Chromatog.* **2**, 605.

TABLE 1. SOLVENT SHIFTS (δ) OF METHOXYL PROTONS

Isoflavone	Chemical shift 6- or 8-OMe $CDCl_3$ (C_6D_6)	4'-OMe $CDCl_3$ (C_6D_6)
7-Acetoxy-8,4'-dimethoxy	3·82 (3·72)	4·00 (3·34)
7,3'-Diacetoxy-8,4'-dimethoxy	3·86 (3·72)	4·00 (3·30)
7,3'-Diacetoxy-6,4'-dimethoxy	3·85 (3·20*)	3·92 (3·30*)
7,8-Diacetoxy-6,4'-dimethoxy	3·84 (3·18†)	3·94 (3·20†)

* Assignment may be reversed.
† Assignment may be reversed.

(**1**; R=R'=H). This was established by direct comparison of the dimethyl ether with authentic material.[2] Retusin and its 8-methyl ether were recently found in the heartwood of *D. retusa.*[2]

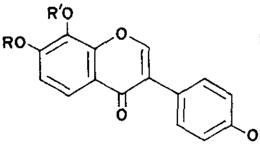
Compound 3, $C_{17}H_{14}O_6$, contained two methoxyl groups, five aromatic protons, and an isoflavonoid 2–H proton (Table 2), and formed a diacetate and a dimethyl ether, one of the hydroxyl groups being located at C-7 (UV). The NMR spectrum of the diacetate is similar to that of (**1**; R=Ac, R'=Me), the AB quartet from the ring A protons being almost identical (Table 2), but the four-proton AB system of the latter is replaced by signals from only three protons in ring B. Further examination of the NMR spectra indicated that the additional substituent in ring B occurred at position-3' suggesting that compound 3

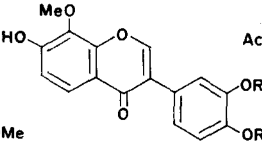
TABLE 2. NMR SPECTRA* OF ISOFLAVONES IN *Dipteryx odorata*

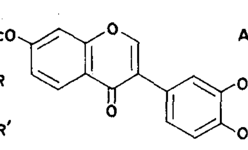
Compound	H-2	H-5	H-6	H-8	H-2'	H-3'	H-4'	H-5'	H-6'
1 (**1**; R=H,R'=Me)	7·95	7·96 *d* (*J* 9)	7·04 *d* (*J* 9)		7·48 *d* (*J* 9)	6·96 *d* (*J* 9)		6·96 *d* (*J* 9)	7·48 *d* (*J* 9)
1-Acetate	8·00	8·02 *d* (*J* 9)	7·10 *d* (*J* 9)		7·48 *d* (*J* 9)	6·96 *d* (*J* 9)		6·96 *d* (*J* 9)	7·48 *d* (*J* 9)
2 (**1**; R=R'=H)‡ (retusin)	8·05	7·64 *d* (*J* 9)	6·96 *d* (*J* 9)		7·45 *d* (*J* 9)	6·96 *d* (*J* 9)		6·96 *d* (*J* 9)	7·45 *d* (*J* 9)
3 (**2**; R'=H,R=Me)§	8·16	7·78 *d* (*J* 9)	6·98 *d*† (*J* 9)		7·03 *d*† (*J* 2)			6·98 *d*†	6·98†
3-Diacetate	8·04	8·00 *d* (*J* 9)	7·12 *d* (*J* 9)		7·31 *d* (*J* 2)			7·03 *d* (*J* 9)	7·42 *dd* (*J* 9 and 2)
3-Dimethyl ether	8·02	8·04 *d* (*J* 9)	7·04 *d* (*J* 9)		7·22 *d* (*J* 2)			6·92 *d* (*J* 8)	7·04 *dd* (*J* 8 and 2)
4 (**5**)§ (odoratin)	8·08	7·52		← — — -7·04–6·86 (*m*, 4H)– — — — — — →					
4-Diacetate	7·97	7·73		7·22	7·29 *d* (*J* 2)			7·02 *d* (*J* 9)	7·42 *dd* (*J* 9 and 2)
4-Dimethyl ether	7·94	7·61		6·86	7·23 *d* (*J* 2)			6·90 *d* (*J* 9)	7·05 *dd* (*J* 9 and 2)
5 (**6**)§ (Dipteryxin)	8·15	7·16			7·44 *d* (*J* 9)	6·94 *d* (*J* 9)		6·94 *d* (*J* 9)	7·44 *d* (*J* 9)
5-Diacetate	7·93	7·65			7·47 *d* (*J* 8)	6·97 *d* (*J* 8)		6·97 *d* (*J* 8)	7·47 *d* (*J* 8)
5-Dimethyl ether	8·00	7·45			7·50 *d* (*J* 9)	6·96 *d* (*J* 9)		6·96 *d* (*J* 9)	7·50 *d* (*J* 9)

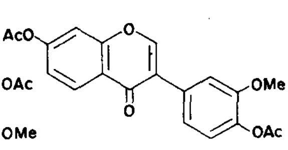
* Values in δ, coupling constants (*J*) in Hz, spectra recorded on Varian HA-100 in $CDCl_3$ unless otherwise stated: *d* = doublet, *dd* = double doublet, *m* = multiplet.
† Overlapping signals, assignment uncertain; see spectrum of the diacetate.
‡ In $CDCl_3/CD_3OD$.
§ In CD_3OD.

dimethyl ether, m.p. 164–165°, is 7,8,3′,4′-tetramethoxyisoflavone (lit.[4] 168–170°), and compound 3 itself is either 7,3′-dihydroxy-8,4′-dimethoxyisoflavone (**2**; R=H, R′=Me) or 7,4′-dihydroxy-8,3′-dimethoxyisoflavone (**2**; R=Me, R′=H). That the former is correct is evident from the NMR spectrum of the diacetate; the lowest field signal of the B ring protons (*δ* 7·42 *dd*), assigned to H–6′, is coupled to H–5′ at *δ* 7·03 (*d*, *J* 9Hz) and to H–2′ at *δ* 7·31 (d, *J* 2Hz). These values agree closely with those of (**3**)[5] (7·42 *dd*, 7·02 *d*, and 7·30 *d*) but are not consistent with those of (**4**).[6] Thus compound 3 is 3′-hydroxyretusin 8-methyl ether (**2**; R=H, R′=Me).

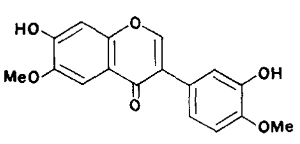

(**1**)

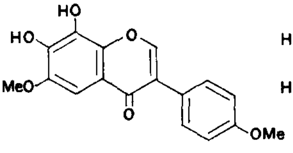

(**2**)

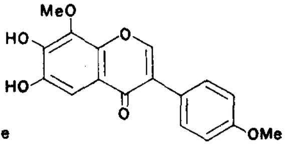

(**3**)


(**4**)

Compound 4, odoratin, is a dihydroxydimethoxyisoflavone isomeric with compound 3. In the NMR spectrum of the diacetate three protons in ring B form an ABX system almost identical with that of the diacetate of compound 3 (**2**; R=Ac, R′=Me, OAc in place of OH) (Table 2). The remaining aromatic proton signals are 1H singlets, that at lowest field (*δ* 7·73) being assigned to H–5 and hence the other (*δ* 7·22) corresponds to H-8. The small UV shift with sodium acetate was actually hypsochromic (cf. afrormosin)[7] but after deuterium exchange, using the method of Kirby and Ogunkoya,[8] the signal at *δ* 6·90 disappeared (as well as two others from ring B) showing that a hydroxyl group is located at C–7. Odoratin is therefore 7,3′-dihydroxy-6,4′-dimethoxyisoflavone (**5**). Direct comparison showed that the dimethyl ether was identical with 6,7,3′,4′-tetramethoxyisoflavone previously isolated[9] from *Cordyla africana*. The 3′-*O*-methyl ether occurs in *Cladastris lutea.*[10]


(**5**)


(**6**)


(**7**)

Compound 5, dipteryxin, is another isomer of compounds 3 and 4. It possesses a 7-hydroxyl group (UV), and a catechol system (molybdate test). The NMR spectrum of the diacetate includes a four proton AB quartet, the same as that from the acetate of compound 1, and a singlet (1H) at *δ* 7·16 which must be assigned to H–5. Thus dipteryxin is either (**6**) or (**7**). Reference to Table 1 shows that in the NMR spectra of the acetates of compounds 1 and 3, the signal from the 8-methoxyl protons is scarcely affected (~0·1 ppm)

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[4] Kukla A. S. and Seshadri, T. R. (1962) *Tetrahedron* **18**, 1443.

[5] Jain, A. C., Lal, P. and Seshadri, T. R. (1969) *Indian J. Chem.* **7**, 305.

[6] Takai, M., Yamaguchi, H., Saitoh, T. and Shibata, S. (1972) *Chem. Pharm. Bull.* **20**, 2488.

[7] Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*, Springer, Berlin.

[8] Kirby, G. W. and Ogunkoya, L. (1965) *J. Chem. Soc.* (*C*) 6914.

[9] Campbell, R. V. M., Harper, S. H. and Kemp, A. D. (1969) *J. Chem. Soc.* (*C*) 1787.

[10] Shamma, M. and Stiver, L. D. (1969) *Tetrahedron* **25**, 3887.

on changing from chloroform to benzene solution, but for the A ring methoxyl signals in the acetates of compounds 4 and 5 the solvent shift is ~0·65 ppm. Dipteryxin is therefore regarded as 7,8-dihydroxy-6,4′-dimethoxyisoflavone (**6**).

EXPERIMENTAL

Extraction of Dipteryx odorata. Finely ground heartwood (420 g) was extracted (Soxhlet) with petrol and then with $CHCl_3$ (2 l.). The residue (4·51 g) from the latter was treated with a little cold $CHCl_3$. The insoluble portion (1·28 g) mainly compounds 2 and 5, was separated by PLC on SiO_2 in EtOAc–MeOH (100:1). The $CHCl_3$-soluble portion (3·23 g) was fractionated by PLC in SiO_2 in $CHCl_3$–EtOH (20:1), the three major bands (compounds 1, 3 and 4) being eluted.

Retusin 8-methyl ether (compound 1) (**1**; R=H, R′=Me) crystallized from MeOH in leaflets (950 mg m.p. 220–221° (lit.[2] 221°), M^+ 298, λ_{max} (MeOH) 255 nm, λ_{max} (MeOH–NaOAc) 265 nm, ν_{CO} (KBr) 1640 cm^{-1}. The acetate crystallized from MeOH in needles, m.p. 122·5–123·5° (lit.[2] 124–125°) identical (IR, TLC, m.m.p.) with 8-*O*-methylretusin acetate. The methyl ether had m.p. 150–151° (lit.[2] 151°).

Retusin (compound 2) (**1**; R=R′=H) crystallized from acetone in cubes (40 mg), m.p. 249–250° (lit.[2] 249°), M^+ 284, λ_{max} (MeOH) 261 nm, λ_{max} (MeOH–NaOAc) 283 nm, ν_{CO} (KBr) 1630(br) cm^{-1}, green colour with $FeCl_3$ and brown with Na_2MoO_4. The dimethyl ether, m.p. 150–151° (lit.[2] 151°) was identical (IR, TLC, m.m.p.) with an authentic specimen.

3′-Hydroxyretusin 8-methyl ether (compound 3) (**2**; R=H, R′=Me), crystallized from MeOH in needles (35 mg), m.p. 208–210° (Found: M^+ 314·0790. $C_{17}H_{14}O_6$ requires 314·0790), λ_{max} (MeOH) 255 nm, λ_{max} (MeOH–NaOAc) 266 nm, ν_{max} (KBr) 3500, 1630, 1610, 1590, 1515 cm^{-1}. *Diacetate*, m.p. 163–165° (from MeOH) (Found: M^+ 398·0998. $C_{21}H_{18}O_8$ requires 398·1001), λ_{max} (MeOH) 256, 315 *sh* nm, ν_{max} (KBr) 1770, 1765 *sh*, 1650, 1615 cm^{-1}. *Dimethyl ether*, m.p. 164–165° (from MeOH) (Found: M^+ 342·1100. $C_{19}H_{18}O_6$ requires 342·1103), λ_{max} (MeOH) 255, 290 *sh* nm, ν_{max} (KBr) 1640, 1600 cm^{-1}.

Odoratin (compound 4) (**5**), (65 mg), was purified via the diacetate. This was hydrolysed by refluxing under nitrogen in EtOH–3 N HCl for 3·5 hr. and the product, after TLC, crystallized from MeOH as needles, m.p. 210–211° (65 mg) (Found: M^+ 314·0790. $C_{17}H_{14}O_6$ requires 314·0790), λ_{max} (MeOH) 260, 290 *sh* nm, λ_{max} (MeOH–NaOAc) 258, 290 *sh*, 338 nm, ν_{max} (KBr) 3400 *br*, 1625, 1585, 1510 cm^{-1}. Deuterium exchange[8] was effected by heating odoratin (8 mg) in D_2O (0·1 ml) with triethylamine (0·3 ml) and dimethylformamide (2 drops) in a sealed tube at 100° for 48 hr. After evaporation to dryness the residue was dissolved in CD_3OD. The NMR spectrum, at low field, showed three singlets at δ 8·08 (H–2), 7·52 (H–5) and 6·94 (H–5′) (cf. Table 2). Dimethyl ether, m.p. 186–187° (lit.[9] 187–188°) was identical (IR, TLC, m.m.p.) with an authentic sample. Acetylation in cold Ac_2O/pyridine and purification by PLC gave the *diacetate*, m.p. 185–187° (from MeOH) (Found: M^+ 398·0998. $C_{21}H_{18}O_8$ requires 398·1001), λ_{max} (MeOH) 260, 330 nm, ν_{max} (KBr) 1780, 1660, 1540, 1500 cm^{-1}.

Dipteryxin (compound 5) (**6**), m.p. 250–254° (from MeOH) (55 mg) (Found: M^+ 314·0789. $C_{17}H_{14}O_6$ requires 314·0790), λ_{max} (MeOH) 266, 325 nm, λ_{max} (MeOH–NaOAc) 280, 340 nm, λ_{max} (MeOH–NaOAc–H_3BO_3) 272, 335 nm, ν_{max} (KBr) 3360br, 1615, 1585, 1555, 1515 cm^{-1}, green colour with $FeCl_3$ and brown with Na_2MoO_4. *Diacetate*, m.p. 170–171° (from MeOH) (Found: M^+ 398·0998. $C_{21}H_{18}O_8$ requires 398·1001), λ_{max} (MeOH) 258, 330 nm, ν_{max} (KBr) 1783, 1650, 1620, 1585, 1515 cm^{-1}. *Dimethyl ether*, m.p. 108° (from MeOH) (Found: M^+ 342·1100. $C_{19}H_{18}O_6$) requires 342·1103), λ_{max} (MeOH) 264, 340sh, ν_{max} (KBr) 1645, 1600, 1575 cm^{-1}.

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