Pergamon

PII: S0031-9422(97)00161-1

Phytochemistry, Vol. 45, No. 7, pp. 1523–1525, 1997

0031-9422/97 $17.00+0.00

7-HYDROXY-2,3,5,6-TETRAHYDRO-3,6,9-TRIMETHYLNAPHTHO[1,8-B,C]PYRAN-4,8-DIONE FROM *THESPESIA POPULNEA*

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(*Received in revised form* 14 *December* 1996)

Key Word Index—*Thespesia populnea*; Malvaceae; Milo wood; mansonones; sesquiterpenoid quinones.

Abstract—A new mansonone, 7-hydroxy-2,3,5,6-tetrahydro-3,6,9-trimethylnaphtho[1,8-b,c]pyran-4,8-dione, in addition to mansonones D, E and F were isolated from the heartwood of *Thespesia populnea* collected in Hawaii. The structure of the new compound was elucidated by means of spectroscopic methods including 2-D-COLOC experiments.

INTRODUCTION

Thespesia populnea (L.) Sol., commonly known as the Portia tree, is widespread in Hawaii, California and Florida, and also in Asia, Africa and the Caribbean Islands. In Hawaii, the heartwood we have investigated is known as the Milo tree [1]. Several mansonones, highly oxidized sesquiterpenes containing a cadinane skeleton, were found in Milo wood (Fig. 1). These sesquiterpenoid quinones are known to induce contact dermatitis in man, to inhibit tumour formation and to have antifungal properties. They also affect lipid peroxidation and cytochrome P450 activity [2–10]. The mansonones C–F as well as thespesone and thespone have been identified from Indian *T. populnea* [11]. We now report on the isolation and structural elucidation of a new mansonone, 7-hydroxy-2,3,5,6-tetrahydro-3,6,9-trimethylnaphtho[1,8-b,c]pyran-4,8-dione, from Hawaiian heartwood, which also affords the mansonones D, E and F.

RESULTS AND DISCUSSION

The new mansonone obtained from powdered heartwood is a manor mansonone constituent of milo wood. Its mass spectrum shows a $[M]^+$ peak of 100% rel. intensity and the absence of an associated $[M+2]^+$ ion signal which is indicative for structures like 1,2- or 1,4-naphthoquinones.

The ^{13}C NMR data of **1** revealed a naphtho[1,8-b,c]pyran skeleton while the ^1H NMR spectrum showed the presence of two secondary methyl groups at δ 1.16 and 1.19. Furthermore, signals of methine protons at δ 3.12 and 3.61 coupled to two pairs of methylene proton resonances located at δ 4.15, 4.28 and at δ 2.60, 2.78 were observed. The presence of two secondary carbons is further confirmed by the ^{13}C NMR data. In addition, the ^1H NMR spectrum of **1** contained a singlet at δ 7.11. After proton exchange, we assigned this signal to a hydroxy group connected to an olefinic carbon which is in accordance with a ^{13}C NMR signal at δ 143.6 (C-7). By means of a 2-D-H,C-COLOC experiment it was shown that only one CO is located next to the hydroxy group. Additional COLOC couplings are illustrated in Fig. 2.

EXPERIMENTAL

^1H and ^{13}C NMR: 500 MHz and 125.8 MHz, respectively, TMS as int. standard. The multiplicity of the ^{13}C NMR signals was determined by DEPT experiments. EI-MS: 311A Varian MAT instrument; CI-MS (NH_3): VG Analytical 70–250 S mass spectrometer.

Plant material. A sample of *Thespesia populnea* heartwood was collected from Hawaii.

Extraction. Powdered heartwood (36 g) was extracted under reflux with $CHCl_3$ for 12 hr. The crude extract was evapd at red. pres. and the residue (3 g) was chromatographed over silica gel (300 g) using toluene (3 l), followed by $CHCl_3$ (2 l) and then Me_2CO (1 l). Two main frs (A and B) were collected. Fr. A was chromatographed over silica gel (15 g) using toluene Me_2CO (20:1 as an eluent and yielded 86 mg

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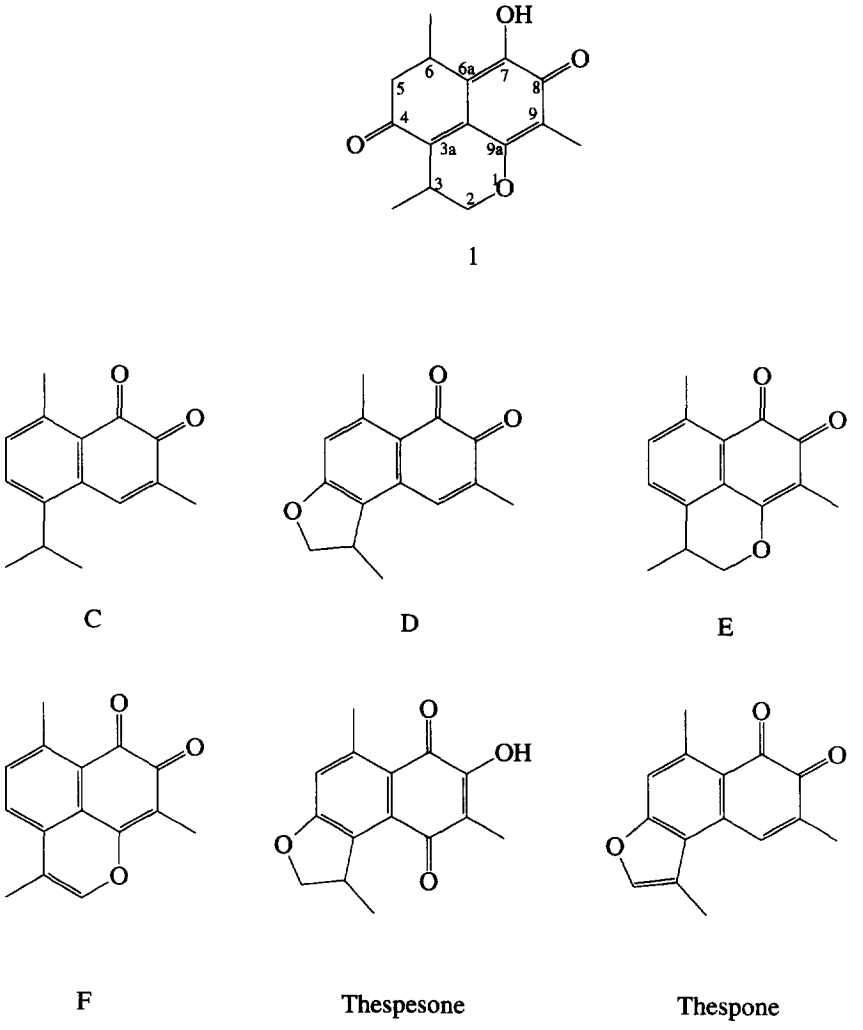

Fig. 1. Mansonones from *T. populnea*.

1. Fr. B was further sepd over silica gel (120 g, toluene–Me_2CO 20:1) and afforded after evapn at red. pres. 55 mg mansonone D, 32 mg mansonone E and 32 mg mansonone F which were identified by reference to literature data.

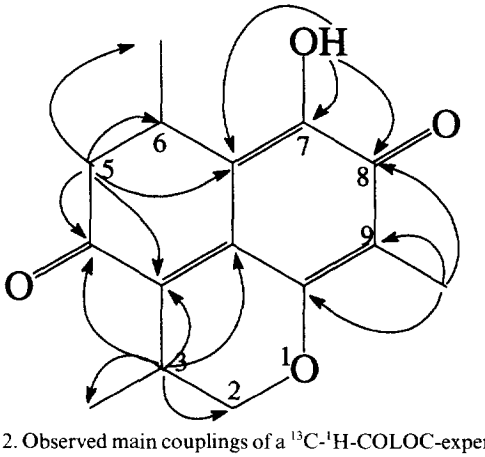

Fig. 2. Observed main couplings of a ^{13}C-^{1}H-COLOC-experiment.

7-Hydroxy-2,3,5,6-tetrahydro-3,6,9-trimethylnaphtho[1,8-*b*,*c*]*pyran-4,8-dione* (**1**). Reddish-brown crystals. ^1H NMR ($CDCl_3$): δ 1.16 (3 H, *d*, $J_{Me,H-3}$ = 7.1 Hz, 3-Me), 1.19 (3 H, *d*, $J_{Me,H-6}$ = 7.1 Hz, 6-Me), 1.94 (3 H, *s*, 9-Me), 2.6 (1H, *dd*, $J_{5a,6}$ = 1.5 Hz, $J_{5a,5b}$ = 16.3 Hz, H-5a), 2.78 (1H, *dd*, $J_{5b,6}$ = 6.6 Hz, $J_{5b,5a}$ = 16.3 Hz, H-5b), 3.12 (1H, *dq*, $J_{3,Me}$ = 7.1 Hz, $J_{3,2a}$ = 3.5 Hz, H-3), 3.61 (1H, *dquint*, *J*6,5a = 1.5 Hz, $J_{6,5b}$ = 6.6 Hz, $J_{6,Me}$ = 7.1 Hz, H-6), 4.15 (1 H, *dd*, $J_{2a,2b}$ = 10.5 Hz, $J_{2a,3}$ = 3.5 Hz, H-2a), 4.28 (1H, *dd*, $J_{2b,2a}$ = 10.5 Hz, $J_{2b,3}$ = 1 Hz, H-2b); ^{13}C NMR ($CDCl_3$, off resonance): δ 7.97 (*q*, 9-Me), 16.18 (*q*, 3-Me), 20.64 (*q*, 6-Me), 143.6 (*s*, C-7), 181.27 (*s*, C-8), 115.04 (*s*, C-9), 115.10 (*s*, C-6a), 157.27 (*s*, C-9a), 131.02 (*s*, C-9b), 139.41 (*s*, C-3a), 197.13 (*s*, C-4), 44.49 (*t*, C-5), 27.54 (*d*, C-6), 26.41 (*d*, C-3), 71.88 (*t*, C-2); MS-EI, *m/z* (rel. int.): 260 ($[M]^+$, 67), 245 (100), 232 (16), 218 (25), 217 (28), 203 (34), 161 (26), 115 (26), 91 (35), 83 (62); MS-CI (ammonia), *m/z* (rel.

int.): 261 $[M+1]^+$ (100). $C_{15}H_{16}O_4$: calcd. 260.1044 found 260.1060 (MS); UV λ_{max}^{MeOH} nm (log ε): 352 (4.17), 339 (4.16), 271 (4.08), 210 (4.19); $[\alpha]_D^{23} = +324$ ($c = 0.1$, $CHCl_3$).

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