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ULMACEAE

SESQUITERPENES FROM THE HEARTWOOD OF CHINESE ELM

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Plant. Ulmus parvifolia JACQ. Occurrence. Taiwan (Formosa). *Uses.* Folk medicinal, diuretic and expectorant. *Previous work.* On sister species, [1–8] reported the occurrence of cadalenic and calamenic sesquiterpenes,[1–4] lignans,[5,6] and phenolic constituents.[7,8]

Present work. Dried and ground Chinese elm wood was extracted with acetone and evaporated. The benzene extract of the residue was chromatographed over a column of SiO_2, eluting with benzene and EtOAc, giving 7-hydroxycadalenal,[1] 3-methoxy-7-hydroxycadalenal,[1] mansonone C,[9] sitosterol, and mansonone G.[10] The structures of the individual components were suggested from the data of IR, UV, NMR, and mass spectra and confirmed by comparison with the authentic samples (TLC, IR, and m.m.p.).

EXPERIMENTAL

Dried and ground Chinese elm wood was extracted with acetone and the solvent removed. The benzene extract of the residue was chromatographed on SiO_2: eluting with benzene yielded a mixture of two crystalline compounds I and II, then another two crystalline compounds III and IV. Further elution with benzene–EtOAc (10:1) yielded compound V. The mixture of compounds I and II were separated by repeated chromatography on SiO_2 eluting with *n*-hexane–benzene (3:2) and then recrystallized with *n*-hexane. The separation of compound III and IV was achieved by elution with *n*-hexane–$CHCl_3$–EtOAc (15:3:2).

Compound I. Yellow needles, m.p. 85° (*n*-hexane), $C_{15}H_{16}O_2$ (M^+ 228); λ_{max}^{EtOH} (log ϵ) 219 (4·29), 244 (4·49), 248·6 (4·66), 254·5 (4·77), 260 (4·75), 312sh (3·97), 400 (3·42) nm; $\lambda_{max}^{EtOH\text{-}NaOH}$ (log ϵ) 238 (4·59), 243 (4·58), 248 (4·65), 254·5 (4·74), 260 (4·73), 269 (4·64), 329 (4·04), 465 (3·55) nm; ν_{max} (KBr) 3200 (OH), 2825, 2700, 1658 (CHO), 1630, 1600, 1580, 1525, 1515 (ar), 1378, 1380 ($CH(CH_3)_2$)cm^{-1}; NMR: δ 1·38 (6H, d, $J = 7$ Hz) and 3·37 (1H, m, $J = 7$ Hz) indicated CH $(CH_3)_2$, 2·58 (3H, s, Me in arom. ring), centered at 7·29 (ABq, $J = 8$ Hz, two adjacent arom. H), 7·43 (1H, s) and 8·43 (1H, s) indicated two isolated arom. H, 10·10 (1H, s, CHO), 10·35 (1H, s, ArOH); MS: *m/e* 229 (M + 1, 13·3%), 228 (M^+, 82·2), 214 (M–CH_2, 100), 186 (214–CO, 9·3), 171 (186-Me, 18·9), 143 (171-CO, 6·3), 142 (171-CHO, 9·2).

Acetate of compound I. Pale yellow needles, m.p. 113–115°; ν_{max} (KBr) 1760, 1200 (CO·O) cm^{-1}, the strong sharp band of compound I at 1658 shifted to 1700 cm^{-1} suggested OH and CHO were in ortho position.

Reduction of compound I with $LiAlH_4$ in ether gave colourless compound, m.p. 140–142°, ν_{max} (KBr) 3355 (OH), 1240 (ArOH), 1030 (1° -OH); NMR: δ 5·03 (2H, s, $C\underline{H}_2OH$). *Acetate*: colourless needles, m.p. 68–70°, ν_{max} (KBr) 1760, 1740, 1224, 1200 (Ar.O.$COCH_3$, Ar.CH_2.O.$COCH_3$) cm^{-1}; NMR: δ 2·10 (3H, s, Ar.CH_2O.$COC\underline{H}_3$), 2·40 (3H, s, Ar $OCOC\underline{H}_3$). From the data presented above, the compound I appeared to be 7-hydroxycadalenal which was confirmed by comparison with an authentic sample (TLC, IR, and m.m.p.).

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Compound II. Golden-yellow needles (*n*-hexane), m.p. 137–139°, $C_{16}H_{18}O_3$, λ_{max}^{EtOH} (log ϵ): 223 (4·12), 239sh (3·94), 243sh (4·05), 249 (4·21), 255 (4·35), 261 (4·41) 419 (2·99) nm; $\lambda_{max}^{EtOH-NaOH}$ (log ϵ) 233 (4·16) 243 (4·10), 249 (4·21), 254·5 (4·34), 260·5 (4·39), 327 (5·94), 470 (3·36) nm; ν_{max} (KBr) 3230 (OH), 2800, 2700, 1660 (CHO), 1610, 1585, 1525, 1455 (arom. ring), 1355, 1375 ($CH(CH_3)_2$) cm^{-1}; NMR: similar to that of compound I, but the signal of AB quartet centered at δ 7·29 of compound I shifted to δ 7·27 (1H, s) and a new singlet appeared at δ 3·95 (3H, Ar–CH_3). 3,5-*Dinitrobenzoate*: pale brown crystals, m.p. 214–216°. From the data presented above the compound II appeared to be 3-methoxy-7-hydroxycadalenal which was confirmed by comparison with an authentic sample (TLC, IR, and m.m.p.).

Compound III. Orange-red needles, m.p. 138–139°, $C_{15}H_{16}O_2$ (M^+ *m/e* 228); ν_{max} (KBr) 1660, 1648 (*o*-quinone CO) cm^{-1}, absence of OH; λ_{max}^{MeOH} (log ϵ) 210 (3·68), 259 (3·78) nm; NMR: δ 2·63 (3H, s, Me in peri position), 2·10 (3H, s, Me on double bond), 1·35 (6H, d, J = 7 Hz) and 3·33 (1H, m, J = 7 Hz) indicated $CH(CH_3)_2$ on arom. ring, centered at δ 7·35 (ABq, J = 9 Hz, two arom. H), 7·70 (1H, s, olefinic H); MS: *m/e* 230 (M + 2, 2·2%), 229 (M + 1, 1·1), 228 (M^+, 1·4), 200 (M-CO, 74·8), 185 (200-Me, 100), 157 (185-CO, 11·6), 142 (185-C_3H_7, 33·3), 115 (157-C_3H_6, 17·2). This feature of the spectrum, the relative intensities of M + 1 and M + 2 peaks were 1·1 and 2·2 respectively, bigger than the calculated values and the M + 2 peak (2·2) was bigger than the M^+ peak (1·4), suggested the presence of *o*-quinone. Further, treatment with *o*-phenylendiamine a quinoxaline derivative, yellow needles, m.p. 105–106°, was obtained which also indicated the presence of *o*-quinone structure. From the above date, it is clear that the compound III must be mansonone C which was confirmed by comparison with an authentic sample (TLC, IR, and m.m.p.).

Compound IV. Colourless plates, m.p. 138–140°, identical (TLC and IR) with authentic sitosterol; *the monoacetate*: m.p. 120°.

Compound V. Orange needles, m.p. 218–219° (benzene), $C_{15}H_{16}O_3$ (M^+ *m/e* 244); ν_{max} (KBr) 3280 (OH), 1658, 1645 (*o*-quinone CO) cm^{-1}; λ_{max}^{MeOH} (log ϵ) 221 (4·34), 239 (4·16), 275 (4·27), 410 (3·93) nm; $\lambda_{max}^{MeOH-NaOH}$ (log ϵ) 232 (4·36), 304 (4·09), 435 (3·63) nm; NMR spectrum was very similar to that of compound III, but the signal of δ 7·35 (AB q, J = 9 Hz) displaced to 6·72 (1H, s) indicated this compound to be a *o*-quinone with OH group; *m/e* 246 (M + 2, 1·9%), 245 (M + 1, 1·5), 244 (M^+, 4·2), 229 (M–Me, 7·3), 216 (M–CO, 52·9), 201 (216-Me, 100), 173 (201-CO, 5·9), 158 (173-Me, 7·4), 115 (158-C_3H_7, 10·1). Treatment with *o*-phenylendiamine afforded a quinoxaline derivative, yellow needles, m.p. 197° (soften), 218–219°.

The monoacetate. Red crystals, m.p. 95–97°, NMR spectrum showed the protons of the acetoxyl group as a singlet at δ 2·40 (3H).

The above feature of the spectrum suggested that the compound V must be mansonone G which was confirmed by comparison with an authentic sample (TLC, IR, and m.m.p.).

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Key Word Index—Ulmus parvifolia; Ulmaceae; sesquiterpenes; cadalenals; mansonones; sitosterol.

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MONOCOTYLEDONAE

AMARYLLIDACEAE

STEROIDAL SAPOGENINS FROM *AGAVE COCUI*

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Plant. Agave cocui. Source. Between Ejido-Las González. Edo. Mérida. Venezuela.