

SHORT COMMUNICATION

AN EXAMINATION OF THREE *QUERCUS* SPECIES OF HONG KONG

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Abstract—From the leaves of the following have been isolated: *Quercus bambusaefolia*: friedelin, friedelan-3 α -ol, friedelan-3 β -ol, β -sitosterol, and a higher alcohol A1; *Q. championi*: the higher alcohol A1, a higher ketone K1; *Q. myrsinaefolia*: friedelan-3 α -ol, friedelan-3 β -ol, β -sitosterol, and the higher ketone K1.

RESULTS AND DISCUSSION

Arthur, Hui, Lam and Szeto reported¹ the occurrence of six triterpenoids including hop-17(21)-en-3 β -ol and its acetyl derivative in the leaves of *Q. championi* of Hong Kong. The hopane derivatives had not previously been isolated from a plant. It was thought that investigations of other *Quercus* species might reveal the presence of similarly interesting triterpenoids. However in the leaves of *Q. bambusaefolia* and *Q. myrsinaefolia* only friedelin and the two friedelanols were encountered among the triterpenoids; β -sitosterol was also obtained from both species. Further work on *Q. championi* leaves revealed the presence of a higher fatty alcohol, A1, resembling *n*-triacontanol but shown by mass spectrometry not to be that alcohol, and a higher fatty ketone, K1. (Mass spectra are under interpretation.) The ketone K1 was also detected in the leaves of *Q. myrsinaefolia* and the alcohol A1 in the leaves of *Q. bambusaefolia*.

EXPERIMENTAL

Microanalyses were made by the Microanalytical Laboratory of the University of Singapore. Alumina used was B.D.H. preparative grade. Light petroleum had b.p. 60–80°. Specific rotations were taken in chloroform; i.r. spectra were taken on a P-E model 137 Infracord spectrophotometer; m.p.'s of triterpenoids were taken on a gas-heated copper block while those of other samples in a paraffin bath. For all known compounds i.r. spectra were found to be identical with those of authentic specimens; and no known compound depressed the m.p. of an authentic sample in a mixed m.p. determination.

Extraction

The dried leaves of each *Quercus* species were extracted with light petroleum as described¹ for *Q. championi*. The green-coloured residues left after distillation of the petroleum were obtained in the following yields: *Q. bambusaefolia* 1.7, *Q. championi* 2.0 and *Q. myrsinaefolia* 1.6 per cent.

¹ H. R. ARTHUR, W. H. HUI, C. N. LAM and S. K. SZETO, *Austral. J. Chem.* 17, 697 (1964).

Isolation of compounds

(a) *Q. myrsinaefolia*. The residue from the petroleum extract (80 g) was redissolved in light petroleum (2 l.) and the solution applied to a column of alumina (1.2 kg). Elution with light petroleum yielded fractions 1–115 (each 500 ml). Elution with light petroleum:benzene (1:1) yielded fractions 161–212 (each 500 ml). The solvent was removed from each fraction, and fractions containing the same substance combined.

(i) *Ketone K1*. Fractions 3–45 yielded a substance which on recrystallization from petroleum gave colourless plates, m.p. 74–76°, shown to be identical with the sample obtained from *Q. championi* reported below.

(ii) *Friedelan-3β-ol*. Fractions 46–115 gave a solid which on crystallization from chloroform yielded friedelan-3β-ol, m.p. 271–273°, $[\alpha]_D +22^\circ$ (*c* 0.38) (Found: C, 83.2; H, 12.2. Calc. for $C_{30}H_{52}O$: C, 84.0; H, 12.2%). A sample was converted into friedelan-3β-yl acetate which on crystallization from benzene had m.p. 289–290° (Found: C, 82.3; H, 11.9. Calc. for $C_{32}H_{54}O_2$: C, 81.6; H, 11.6%).

(iii) *Friedelan-3α-ol*. The solid from fractions 161–180 on crystallization from petroleum yielded friedelan-3α-ol, m.p. 288–291°, shown to be identical with a sample from *Q. championi*.

(iv) *β-Sitosterol*. Fractions 200–212 after collection and recrystallization from ethanol yielded β-sitosterol, m.p. 134.5°, $[\alpha]_D -37.2$ (*c* 0.32) (Found: C, 82.6; H, 12.1; M, 353. Calc. for $C_{29}H_{50}O$: C, 84.0; H, 12.2%; M 417). A sample was converted into β-sitosteryl 3,5-dinitrobenzoate which, after crystallization from ethanol, had m.p. 209–211°.

(b) *Q. bambusaeifolia*. The green mixture (50 g) was chromatographed as stated in (a). Fractions (500 ml) 1–98 were eluted with petroleum; fractions (500 ml) 135–150 were eluted with light petroleum:benzene (1:1).

(i) *Alcohol A1*. Fractions 1–6 on recrystallization from petroleum yielded scintillating plates of *alcohol A1*, m.p. 84–85.5° (Found: C, 81.5; H, 14.6%) identical with a sample from *Q. championi* fully reported upon below.

(ii) *Friedelin*. Fractions 13–23 on crystallization from benzene yielded friedelin, m.p. 250–252° (Found: C, 83.8; H, 12.0. Calc. for $C_{30}H_{50}O$: C, 84.4; H, 11.8%).

(iii) *Friedelan-3β-ol*. Fractions 24–53 on crystallization from methanol yielded friedelan-3β-ol, m.p. 269–272°, $[\alpha]_D +21.3$ (*c* 0.41) (Found: C, 84.2; H, 12.3. Calc. for $C_{30}H_{52}O$: C, 84.0; H, 12.2%). A sample was characterized as friedelan-3β-yl acetate, m.p. 284–287° (from benzene). (Found: C, 82.0; H, 11.8. Calc. for $C_{32}H_{54}O_2$: C, 81.6; H, 11.6%).

Friedelan-3α-ol. Fractions 60–72 on crystallization from petroleum yielded friedelan-3α-ol as shown by its i.r. spectrum.

β-Sitosterol. Fractions 135–150 after collection and five recrystallizations from ethanol yielded β-sitosterol, m.p. 136–137.5° (Found: C, 83.7; H, 12.7. Calc. for $C_{29}H_{50}O$: C, 84.0; H, 12.2%).

(c) *Q. championi*. The green mixture (54 g) was chromatographed as stated in (a). Elution with petroleum yielded 88 fractions, each of 500 ml.

(i) *Alcohol A1*. Fractions 46–88 were recrystallized twice from methanol then once from petroleum and once from acetone from which scintillating plates of *alcohol A1*, m.p. 86.6°, were obtained. (Found: C, 82.1; H, 14.2%; M (Rast) 405. $C_{30}H_{62}O$ required: C, 82.1; H, 14.2%; M 438). γ_{max} 3310 cm^{-1} (OH). A sample was characterized as the acetate which,

after crystallization from methanol, had m.p. 72–73° (Found: C, 79.3; H, 13.6. Calc. for $C_{32}H_{64}O_2$: C, 79.9; H, 13.4%). γ_{max} 1720, 1230 cm^{-1} (—OAc) and the *benzoate*, which after crystallization from methanol had m.p. 67–68° (Found: C, 81.1; H, 12.4. Calc. for $C_{37}H_{66}O_2$: C, 81.9; H, 12.3%). γ_{max} 1700, 1275, 1115 cm^{-1} (PhCOO—).

(ii) *Ketone K1*. Fractions 3–12 were combined and after recrystallization several times from petroleum, methanol then acetone, *ketone K1* m.p. 74° separated (Found: C, 82.2; H, 14.1%; M (Rast) 500. $C_{30}H_{60}O$ required: C, 82.5; H, 13.9%; M 437) γ_{max} 1710 cm^{-1} (C=O).

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