(15%) (ber. für $C_{17}H_{18}O_5$ 302.115); $-CH_2=C=O$ 260 (61); 260 $-CH_2=C=O$ 218 (63); Me CO^+ 43 (100).

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THREE MONOHYDROXYCOUMARINS FROM *ALYXIA LUCIDA*

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Key Word Index—*Alyxia lucida*; Apocynaceae; 3-hydroxycoumarin; 5-hydroxycoumarin; 8-hydroxycoumarin; scopoletin; coumarin.

Alyxia lucida (Cha-loot in Thai) is a fragrant climber of South and Southeast Asia. Dried stem, available in all herbal drug-stores in Thailand, is used medicinally; it is also an essential ingredient of incense.

Successive solvent extractions of dried stems with petrol and chloroform gave mixtures of coumarins. The petrol extract contained coumarin (main constituent), 3-hydroxycoumarin (**1**), and triterpenes. The chloroform fraction yielded scopoletin (**2**) 8-hydroxycoumarin (**3**) and 5-hydroxycoumarin (**4**). These structures were proved by direct comparison with authentic compounds, scopoletin being obtained commercially and the others being synthesized [1–3].

While scopoletin and coumarin are known to be widely occurring in plants, the three monohydroxy coumarins reported in *Alyxia* have not been found before.

EXPERIMENTAL

Air-dried, small stems (< 1 cm diameter) with bark were chopped into fine pieces before extracted successively in Soxhlet with petrol (bp 50–70°) and $CHCl_3$. Extraction by each solvent (15 l./5 kg) was carried out continuously for 25–30 hr. The extracts were evapd to dryness. The dry petrol-extract (2% of dry stem) was boiled with MeOH, the insoluble portion contained several triterpenes one of which was identified as 11-keto-amyrin acetate. The MeOH soluble part was evapd dry and redissolved in minimum vol. of boiling petrol. On cooling, a small amount of ppt. appeared; it was recrystallized from H_2O as colourless needles mp 153–155° (120 mg/kg). MS *m/e* (rel. int.): 162 M^+ (100), 134 (M-CO, 26), 106 (M-2 × CO, 37), 78 (71). Found: C, 67.0; H, 3.6; O, 29.3. Cal. for $C_9H_6O_3$: C, 66.7; H, 3.7; O, 29.6%. ν_{max}^{nujol}: 3300, 1680, 1640, 1600, 1240, 1150 cm^{-1}; λ_{max}^{MeOH} nm (log ε): 288 (4.03), 310 (4.07). NMR (60 MHz, DMSO-d_6, TMS): δ 7.17 (1H, *s*, C-4), 7.68–7.22 (4H, *m*, C-5 to 8), 3.33 (1H, *bs*, exchangeable with D_2O, OH). It was identical with authentic 3-hydroxycoumarin (mmp, IR, NMR and UV). The filtered petrol solution yielded coumarin (1–2 g/kg, mp 67–68°) identical to authentic compound in all respects. The solvent-free $CHCl_3$-extract (3%) was extracted repeatedly with boiling C_6H_6 (until no soluble component remained, checked by TLC). The soln was filtered after re-boiling, evapd dry, redissolved in $CHCl_3$ and chromatographed on Si gel column ($CHCl_3$ and $CHCl_3$–MeOH). Some coumarin and 3-hydroxycoumarin were eluted first, followed by scopoletin, 8-hydroxycoumarin, and 3-hydroxycoumarin. The one identified as scopoletin had mp 203–205° (200 mg/kg stem). ν_{max}^{nujol} cm^{-1}: 3200, 1670, 1600, 1265, 1150; λ_{max}^{MeOH}: 297 (3.68), 345 (4.04); NMR (Py-d_5): δ 6.28 (1H, *d*, *J* = 9.5, C-3), 7.70 (1H, *d*, *J* = 9.5, C-4), 7.10 (1H, *s*, C-5), 7.05 (1H, *s*, C-8), 10.2 (1H, *bs* disappeared after D_2O, OH), 3.79 (3H, *s*, OMe). Found: C, 62.47; H, 4.23; O, 33.30; MW 192. Cal. for $C_{10}H_8O_4$: C, 62.50; H, 4.17; O, 33.33%. It was identical with authentic scopoletin. The one identical with authentic 8-hydroxycoumarin had mp 157–160° (65 mg/kg). ν_{max}^{nujol}: 3390, 1710, 1620, 1550, 1375, 1190; λ_{max}^{MeOH}: 251 (4.15), 289 (4.26). NMR (DMSO-d_6): 6.48 (1H, *d*, *J* = 10, C-3), 8.05 (1H, *d*, *J* = 10, C-4), 7.18 (3H, *s*, C-5, 6, 7), 11 (1H, *bs* disappeared after D_2O, OH). MS: 162 M^+ (100), 134 (M-CO, 100), 106 (M-2 × CO, 15), 78 (47). Found: C, 65.68; H, 3.62; O, 30.7. Cal. for $C_9H_6O_3$: C, 66.7; H, 3.7; O, 29.6%. The one identical with authentic 5-hydroxycoumarin had mp 220–222° (90 mg/kg); ν_{max}^{nujol}: 3200, 1690, 1610, 1190, 1125, 1045; λ_{max}^{MeOH}: 298 (4.14); NMR (DMSO-d_6): δ 6.35 (1H, *d*, *J* = 10, C-3), 8.18 (1H, *d*, *J* = 10, C-4), 6.80 (1H, *d*, *J* = 9, C-6 or 8), 6.81 (1H, *d*, *J* = 9, C-6 or 8), 7.44 (1H, *t*, *J* = 9, C-7), 8.7 (1H, *bs*, OH). MS: 162 M^+ (100), 134 (100), 106 (18), 78 (90). Found: C, 67.13; H, 3.56; O, 29.31. Cal. for $C_9H_6O_3$: C, 66.7; H, 3.7; O, 29.6%.

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