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Phytochemistry, 1977, Vol. 16, pp. 1450-1451. Pergamon Press. Printed in England.

Obwohl *p*-Hydroxyacetophenon-Derivate bei Compositen sehr verbreitet sind [2], hat man derartige Substanzen aus Vertretern der Tribus *Anthemideae* noch nicht isoliert.

(15%) (ber. für $C_{17}H_{18}O_5$ 302.115); $-\text{CH}_2=\text{C}=\text{O}$ 260 (61); 260 $-\text{CH}_2=\text{C}=\text{O}$ 218 (63); Me CO^+ 43 (100).

Anerkennung—Der Deutschen Forschungsgemeinschaft danken wir für die Förderung dieser Arbeit, Herrn Prof. Dr. K. Praefcke für die Beschaffung des Pflanzenmaterials.

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THREE MONOHYDROXYCOUMARINS FROM *ALYXIA LUCIDA*

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(Received 8 March 1977)

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 (151/5 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 $\times$ CO, 37), 78 (71). Found: C, 67.0; H, 3.6; O, 29.3. Cal. for $\text{C}_9\text{H}_6\text{O}_3$: C, 66.7; H, 3.7; O, 29.6%. $\nu_{\text{max}}^{\text{petrol}}$: 3300, 1680, 1640, 1600, 1240, 1150 cm^{-1} ; $\lambda_{\text{max}}^{\text{MeOH}}$ 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). $\nu_{\text{max}}^{\text{petrol}}$ cm^{-1} : 3200, 1670, 1600, 1265, 1150; $\lambda_{\text{max}}^{\text{MeOH}}$: 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 $\text{C}_{10}\text{H}_8\text{O}_4$: 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). $\nu_{\text{max}}^{\text{petrol}}$: 3390, 1710, 1620, 1550, 1375, 1190; $\lambda_{\text{max}}^{\text{MeOH}}$: 251 (4.15), 289 (4.26). NMR (DMSO- d_6): δ 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 $\times$ CO, 15), 78 (47). Found: C, 65.68; H, 3.62; O, 30.7. Cal. for $\text{C}_9\text{H}_6\text{O}_3$: C, 66.7; H, 3.7; O, 29.6%. The one identical with authentic 5-hydroxycoumarin had mp 220–222° (90 mg/kg); $\nu_{\text{max}}^{\text{petrol}}$: 3200, 1690, 1610, 1190, 1125, 1045; $\lambda_{\text{max}}^{\text{MeOH}}$: 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 $\text{C}_9\text{H}_6\text{O}_3$: C, 66.7; H, 3.7; O, 29.6%.

Acknowledgements—We thank Dr. J. Weisbach and J. E. Zarembo of Smith-Kline & French, Philadelphia, U.S.A. for all MS reported here and Dr. Yodhatai Thebtaranondh of Chemistry Department, Faculty of Science, Mahidol University for valuable help. This work was supported by grants from The Rockefeller Foundation and National Research Council of Thailand.

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