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COUMARINS OF LIGUSTICUM ELATUM

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Plant. Ligusticum elatum (Voucher specimen No. 11756/71 deposited at Plant Survey Division, R.R.L.). Previous work. Essential oil [1]. Coumarins [2].

Present work. Air dried roots were extracted with light petrol. (60–80°). The extract revealed the presence of at least seven coumarins on TLC. The presence of anomalin, trans- and cis-khellactones as reported by Kapoor et al. [2] has been confirmed. We report here the isolation of four more known but rare coumarins—three pyranocoumarins of the dihydroseselin type and one linear furanocoumarin.

The petroleum extract was chromatographed on neutral alumina (grade III). Elution with petroleum yielded successively a waxy mass, anomalin (1) (0.05%) and pteryxin (2) $C_{21}H_{22}O_7$ (ca 1.5%), m.p. 80–81° (from petrol-benzene), $\lceil \alpha \rceil_D^{30} + 14^\circ$ (c. 1% in EtOH); v_{max} 1750, 1635, 1621, 1585, 1501, 1320, 1120, 1105, 907, 844, 837 cm⁻¹. NMR (CDCl₃): δ 1.47 (6H, s, gem dimethyl); 1.95 (6H, 2 angelate methyls); 2.1 (3H, s, acetate methyl); 5.32 (1H, d, J 5 cps, H_1); 5.95 (1H, m, olefinic proton of angelate side chain); 6.21 (1H, d, J 9.5 cps. H_A); $6.74(1H, d, J 5 cps; H_1); 6.8(1H, d, J 8.5 cps, H_D);$ 7.39 (1H, d, J 8.5 cps, H_c); 7.58 (1H, d, J 9.5 cps, H_B). Alkaline hydrolysis gave acetic and angelic acids. (PC); acid hydrolysis with 7% H₂SO₄ in 25% aq. HOAc for 3 hr gave cis- and trans-khellactones [3].

The waxy mass on separation by preparative TLC on silica gel G using C_6H_6 -acetone (19:1) afforded selinidin (3) $C_{19}H_{20}O_5$, m.p. 99-100° (acetone petrol) (0·005%). NMR (CDCl₃): δ 1·38 (6H. s, gem dimethyl); 1·92 (6H. m. two olefinic methyls of side chain), 3·1 (2H, m. two benzylic protons); 5·18 (1H. t, H₁): 6·11 (1H, d, J 9·5 cps,

 H_A); 6·68 (1H, d, J 8·5 cps. H_D); 7·2 (1H, d, J 8·5 cps. H_C); 7·55 (1H, d, J 9·5 cps. H_B); 5·97 (1H, m, olefinic proton).

- (1) R = R' = -0 CO C(Me) = CHMe
- (2) R = -0 CO Me; R' = -0 CO C (Me) = CHMe
- (3) R = -0 CO C(Me) = CHMe; R' = H
- (4) R = -0 CO Me; $R' = -0 CO C(Me)^{0} CH(Me)^{0}$

Elution with petrol- C_6H_6 (2:1) afforded bergapten, m.p. $184-85^\circ$ (acetone-petrol) (0·001%) (Co-TLC with authentic sample, IR and NMR spectra) and a gummy mass which on separation by PTLC on silica gel G. using C_6H_6 -acetone (9:1) yielded an oil, R_f : 0·66 on silica gel G. C_6H_6 acetone (9:1), which could not be crystallized. This was identified as epoxypteryxin (4) (Co-TLC with authentic sample prepared by epoxidation of pteryxin with perbenzoic acid). NMR: δ 1·15 (3H. d, oxyangelate methyl d), 2·87 (1H, d, oxyangelate H). Rest of the spectrum was similar to that of pteryxin.

Elution with C_6H_6 -chloroform (1:1) afforded *cis*- and *trans*-khellactones.

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