been considered to be phytoalexins in the heartwood of several coniferous trees [12], this paper and that of Ingham [2] are the first to report such compounds as phytoalexins in herbaceous plants.

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PYRANO FLAVANONE FROM *MILLETIA OVALIFOLIA* SEEDS

Rajinder Kumar Gupta and M. Krishnamurti
Department of Chemistry, University of Delhi, Delhi-110007, India

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Key Word Index—*Milletia ovalifolia*; Leguminosae; pongapin; pongamol; new pyranoflavanone.

Plant. Milletia ovalifolia (Leguminosae). *Past work.* On leaves and bark [1], on seeds [2], on related species [3,4]. *Present work.* On seeds obtained from L. R. Brothers (Saharanpur), India. In continuation of our earlier work [2] further examination of the seeds led to the isolation of pongapin [5], pongamol [6] and a new pyranoflavanone designated as ovalichromene. It crystallized from C_6H_6–petrol as white needles mp 162–163°, $[\alpha]_D^{20}$ −90° and had a formula $C_{21}H_{20}O_4$ (M^+ 336). It gave a Mg/HCl colour reaction, λ_{max}^{MeOH} nm (log ϵ), 255 (4.19), 315 (3.64), 345 (3.56), ν_{max}^{KBr} 1620, 1450, 1320, 1275, 1150, 755, 730 cm^{-1}. PMR (δ values solvent $CDCl_3$) showed a single OMe group at 4.0 (*s*, 3 H); two sharp aromatic proton peaks at 7.5 (*s*, 1 H) (H-5) and 7.65 (*s*, 5 H) (C_6H_5); two doublets at 6.85 (1 H, $J_{3',4'}$ 10 Hz) and 5.75 (1 H, $J_{3',4'}$ 10 Hz) due to $H_{4'}$ and $H_{3'}$; one aliphatic proton at 5.6 (*m*, H-2); two protons at 3.0 (*m*, H-3 proton) and a sharp singlet at 1.55 (6 H, $-C(Me)_2-O-$). These data indicated a close relationship to the flavanone obtained by cyclization of flemichapparin-A [7] and led to the structure of ovalichromene as 6-methoxy-7,8-(2″,2″-dimethylpyrano (5″,6″)-flavanone.

A synthetic sample was prepared from 2,4-dihydroxy-5-methoxy acetophenone by reaction with 3-methyl-3-chloro-but-1-yne in dioxan–K_2CO_3 when 6-acetyl-5-hydroxy-8-methoxy-2,2-dimethyl chromene was obtained as pale yellow needles mp 82–83°; $C_{14}H_{16}O_4$; λ_{max}^{MeOH} nm (log ϵ) 255 (4.31), 320 (3.81), 340 (3.74); ν_{max}^{KBr} 3450 (*b*), 1620, 1445, 1375, 1280, 1140, 980, 890 cm^{-1}. PMR(δ values, CCl_4) 7.3 (*s*, 1 H, H-6), two doublets at 7.05 (1 H, *J* 10 Hz) and 5.8 (1 H, *J* 10 Hz) due to two vinylic protons; three sharp singlets at 4.0 (3 H, –OMe), 2.6 (3 H, –COMe) and at 1.6 (6 H, $-C(Me)_2-O-$); chelated –OH appears at (*s*, 12.55) ($+D_2O$ exchangeable). Treatment of the above chromenoketone with benzaldehyde under basic conditions yielded the chalcone and the corresponding flavanone, ovalichromene, which were separated by TLC on Si gel. The chalcone was obtained as orange-red needles mp 106–108°, $C_{21}H_{20}O_4$, λ_{max}^{MeOH} nm (log ϵ), 300 (4.02), 355 (3.89); ν_{max}^{KBr} 3550 (*br*, 1640, 1570, 1470, 1280, 1150, 960, 885, 760 cm^{-1} PMR (δ CCl_4) showed one –OMe at 3.9 (*s*, 3 H) and one chelated –OH at 12.8 (*s*, 1 H) ($+D_2O$ exchangeable), one sharp singlet at 7.55 (1 H, H-6′), multiplet from 7.7–8.15 (7 H) due to $-C_6H_5$ and α, β-protons and one sharp singlet at 1.6 (6 H–$C(Me)_2-O-$). The IR spectrum (in $CHCl_3$) of the synthetic sample was identical with that of the natural product.

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