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LONG-CHAIN SUBSTITUTED CHROMONES FROM TWO DIANELLINAE

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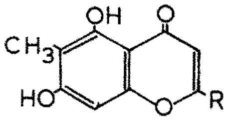
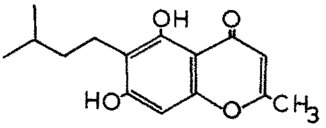
Chromatography of petroleum extracts of roots of both Dianella revoluta and Stypandra grandis has yielded a series of compounds of general structure (I), where R = $C_{27}H_{55}$(n), $C_{29}H_{59}$(n), or $C_{31}H_{63}$(n). The compounds were characterised as a mixture of homologues, and structures have been assigned on the basis of the evidence below.


I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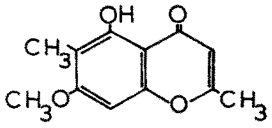
III

Compounds (I) give an intense purple colour with ethanolic $FeCl_3$, as is typical for 5-hydroxychromones[1]. The homologues show absorption maxima at 232, 254(sh), 260 and 301 mμ, (log ε 4.4, 4.25, 4.3 and 4.1), and minima at 244 and 276 mμ (log ε 4.2 and 3.9). These values compare very closely with those for dihydropeucenin (II), but differ significantly from values for analogous 8-alkylchromones[2].

The infrared spectrum of compounds (I) show strong aliphatic absorption, and strong bands at 1645 and 1625 cm^{-1}, close to recorded values for chromones[1]. Mass spectrometry shows three compounds $C_{37}H_{62}O_4$, $C_{39}H_{66}O_4$ and $C_{41}H_{70}O_4$ which lose fragments $C_{25}H_{51}$, $C_{27}H_{55}$ and $C_{29}H_{59}$ respectively to yield a common daughter ion $C_{12}H_{11}O_4^{+}$(m/e 219) or alternatively lose fragments $C_{26}H_{52}$, $C_{28}H_{56}$ and $C_{30}H_{60}$ to yield the common daughter ion $C_{11}H_{10}O_4^{+\cdot}$ (m/e 206). Analogous principal fissions have been observed in the spectrum of 2-heptadecylchromone and other chromones containing extended aliphatic substituents in the 2-position[3].

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The n.m.r. spectrum (recorded in DMSO-D_6) is compatible with structure (I), and the absorptions are tabulated below. The single polymethylene absorption (8.75 τ) demonstrates the normal nature of the alkyl side-chain.

Position of proton(s)	3	5	6	7	8	α-CH_2	-$(CH_2)_n$-	w-CH_3
Chemical shifts (τ)	4.11	-2.8	8.03	6.5	3.66	7.50	8.75	9.15
Multiplicities	si.	si.	si.	brd.	si.	tr.	si.	tr.
Relative intensities	1	1	3	1	1	2	~50	3

Methylation with dimethyl sulphate (in acetone over anhydrous K_2CO_3) gave only the mono ethers (3-proton singlet at 6.14τ instead of broad singlet at 6.5τ, 1-proton singlet at -2.8τ persists). 5-hydroxychromones are known to be very resistant to methylation[1]. These methyl ethers show ultraviolet absorption almost identical to that for eugenitin (III)[2]. Acetylation of the ethers (Ac_2O/Et_3N) gives the 5-acetoxy derivatives (3-proton singlet, 7.62 τ); similar treatment of the parent compounds yields the 5,7-diacetates, which show 3-proton singlets at 7.50 and 7.58τ.

Base hydrolysis of the natural products yields (inter alia) methyl heptacosyl ketone and homologous methyl ketones, a reaction analogous to the recorded formation of acetone from various 2-methylchromones[1]. The synthesis of 5-hydroxy-7-methoxy-6-methyl-2-heptadecylchromone (from 2-hydroxy-4,6-dimethoxyacetophenone, ethyl stearate, NaH/pyridine; HI/HOAc; CH_3I, MeOH/$NaOCH_3$) allowed comparison of this material with the mono-methyl ethers of compounds (I); the n.m.r. spectra were identical except for the intensity of absorption at 8.75τ.

Demethylation of the 7-methoxy compound for direct comparison with the natural products was not undertaken because of ambiguities arising from the recorded tendency for 6-alkylchromones to ring-open and rearrange to the isomeric 8-alkylchromones under acid conditions[1].

To the best of our knowledge, all chromones previously described possess only methyl or hydroxymethyl substituents in the 2-position. Dean and coworkers[4] have recently proposed a rationale for this apparent limitation. It involves the incorporation of an isoprene unit into the phloroglucinol nucleus, and cyclisation after removal by oxidation of one of the carbon atoms. In the light of these new additions to the chromone family, which are almost certainly acetate derived, it seems likely that an acetate derivation will apply to other chromones also, though obviously not necessarily to all.

References

1. F.M.Dean ; "Natrally Occurring Oxygen Ring Compounds", Butterworths, London, 1963
2. A.Bolleter, K.Eiter, H.Schmid ; Helv. chim. acta 34, 186, (1951)
3. J.G.Down ; Ph.D. Thesis, University of Melbourne, 1968
4. F.M.Dean, B.Parton, N.Somvichien, D.A.H.Taylor ; Tetrahedron Letters 1967, 3459