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Swietenone, the first natural *t*-butyl ketone, from *Chloroxylon swietenia*.*

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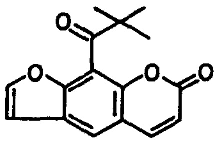
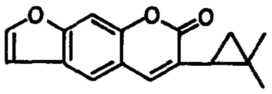
Several coumarins and furoquinoline alkaloids have been reported earlier from *Chloroxylon swietenia* DC (Rutaceae).[1,2] A benzene extract of the bark of a log obtained from Kalghatgi (Karnataka State) has now yielded a new coumarin, swietenone (I), m.p. 160-61°, $C_{16}H_{14}O_4$ ($M.^+$ 270), λ_{max}^{EtOH} 232, 239, 267, 277, 302 nm (log ε 4.47, 4.42, 4.15, 4.15, 3.93), $\nu_{max}^{CHCl_3}$ 1720 cm^{-1} (broad band), shows in its NMR spectrum (chemical shifts on the τ scale) in $CDCl_3$ the characteristic absorptions for a furocoumarin: doublets (*J*=10 Hz) at 2.4 (4-H) and 3.64 (3-H) and doublets (*J*=2 Hz) at 2.41 (2'-H) and 3.31 (3'-H). A linear furocoumarin as in (I), rather than the angular isomer, is favoured by the chemical shift of 3'-H, which appears about 0.5 ppm downfield in the latter.[3] Further the NMR spectrum shows a single-proton singlet at 2.6 (5-H) and a nine-proton singlet at 8.5 which has to be assigned to a *t*-butyl group. A pivalyl group is therefore attached in the 8-position of a furocoumarin, confirmed by the mass spectrum which shows the loss of a C_4H_9 fragment from the molecular ion to give a strong peak at m/e 213.



(I)



(II)

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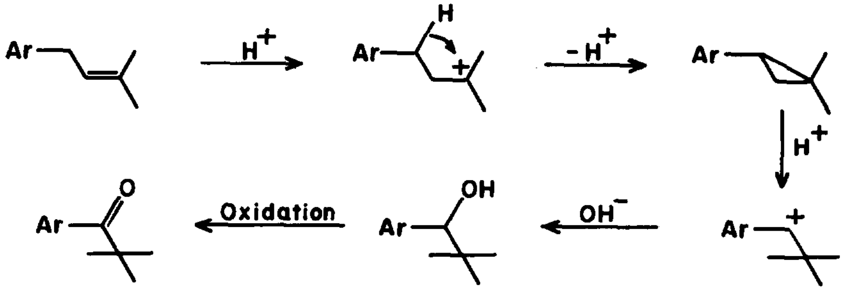
Swietenone is the first natural product with a t-butyl ketone group. Nakanishi et al.[4] identified the terpenoids, ginkgolides and bilobalide (occurring in Gingko biloba), as the first natural products with a t-butyl group. The origin of the t-butyl group was proved by Nakanishi and Habaguchi[5] by incorporating labelled methionine and showing that the radioactivity is located exclusively in the pivalic acid obtained by oxidation. However, since isoprenoid substituents are frequently encountered among coumarins (in Rutaceae plants in particular), the formation of the pivalyl group directly from a C_5 unit can be postulated as shown below.



Very recently Joshi et al.[6] isolated from Clausena indica a new furocoumarin, clausindine (II), in which "the ubiquitous isoprenoid unit is attached to the aromatic nucleus as a gem-dimethylcyclopropane grouping."

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REFERENCES

1. P.S. Kalyanaraman and B.R. Pai, Ind.J.Chem. 10, 2647 (1972).
2. J. Vrkoč and P. Sedmera, Phytochem. 11, 2647 (1972).
3. T.J. Batterham and J.A. Lamberton, Aust.J.Chem. 17, 1305 (1964).
4. K. Nakanishi et al., Tetrahedron Letters 315 (1967); J.Amer.Chem.Soc. 93, 3544 (1971).
5. K. Nakanishi and K. Habaguchi, J.Amer.Chem.Soc. 93, 3546 (1971).
6. B.S. Joshi, V.N. Kamat and D.H. Gawad, Experientia 30, 223 (1974).