Structure of Dregeanin and Rohitukin, Limonoids from the Subfamily *Melioideae* of the Family *Meliaceae*. An Unusually High Absorption Frequency for a Six-Membered Lactone ring

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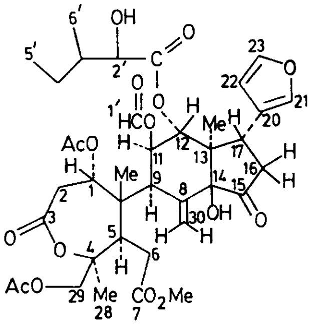
Summary A new group of limonoids, characterised by the possession of a seven-membered lactone ring A, a seco-ring B, and a five-membered carbocyclic ring D, has been discovered in the sub-family *Meliodieae;* a C(1)–C(7) lactone occurring in certain of these is characterised by an unusually high frequency carbonyl absorption in the i.r. spectra.



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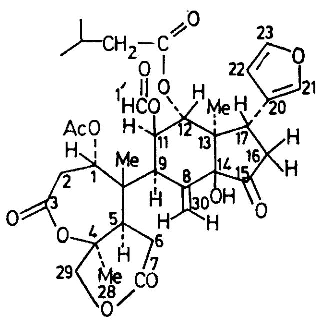

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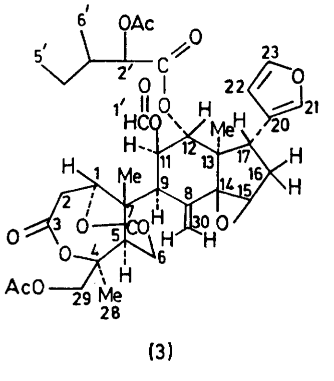

(3)

In our investigations of extractives of the family *Meliaceae,* we have isolated a number of complex, highly-oxidised limonoids, which show obvious similarities. The structure of one of these, prieuranin (**1**) from *Trichilia prieuriana* has already been described.[1] We now describe two more which have interesting structural variations. The first, rohitukin, (**2**), has been isolated from the seed of *Aphanamixis polystacha* (Sanskrit name rohituka) while the second, dregeanin, (**3**), is of wide occurence,[2] and has been isolated either as dregeanin or deacetyldregeanin from *Trichilia dreageana, T. heudelotti, Guarea thompsonii,* and related species. Rohitukin, m.p. 275—280 °C (decomp.) $[\alpha]_D$ $-31°$, $C_{34}H_{42}O_{13}$, has a ^{1}H n.m.r. spectrum very similar to that of prieurianin, and like that of prieurianin it is badly resolved at room temp. but sharpens on warming. Quantitative hydrolysis[3] gives 1 mol each of formic acid, acetic acid, and 3-methylbutyric acid, and shows the presence of two lactone rings. A study of the ^{1}H n.m.r. and ^{13}C n.m.r. spectra show the presence of all the structural elements of prieurianin except that the acid substituted at C-12 is different, and the methyl ester and one of the acetate groups are missing, their place being taken by the second lactone ring. The lactone can extend from C-7 to either C-1 or C-29; the acetate being at the other of these positions. It is not obvious how to show which is the correct structure; partial hydrolysis experiments lead to complex results, in which lactone isomerisation can be shown to have occurred.

Dregeanin, m.p. 264—266 °C, $[\alpha]_D - 6°$, $C_{37}H_{46}O_{14}$, gave 6 mol equiv. of acid on hydrolysis; these were identified as being due to 2 lactones, 2 mol of acetic acid, 1 mol of formic acid, and 1 mol of 2-hydroxy-3-methylvaleric acid. This last occurs also in prieurianin and in the heudelottins.[2] The ^1H n.m.r. spectrum of dregeanin, like that of rohitukin and prieurianin, was only well resolved on warming to *ca.* 45 °C; comparison of the ^1H and ^{13}C n.m.r. spectra of dregeanin and prieurianin then revealed that dregeanin lacked the tertiary hydroxy and cyclopentanone groups present in the other, and had instead an oxide ring of the type familiar from heudelottin and other limonoids.[2] Aside from this the structural elements are similar in all three compounds. The extra acetate in dregeanin can be located at C-2′ of the esterifying acid; as in rohitukin there is a lactone from C-7 to C-1 or C-29, and an acetate at the alternative position.

The lactone systems in dregeanin and rohitukin showed some interesting differences:

(1) In the i.r. spectrum, dregeanin shows carbonyl bands at *ca.* 1740 cm^{-1} (unresolved) and at 1787 cm^{-1} (in $CHCl_3$). Rohitukin does not show the high carbonyl absorption, which implies a strained lactone ring.

(2) Although all these compounds are sensitive to alkaline hydrolysis, dregeanin possesses an especially unstable lactone ring, since on hydrogenation in methanol solution, the production of an 8:30-dihydro-derivative is accompanied by methanolysis of a lactone ring, and disappearance of the 1787 cm^{-1} absorption band.

We therefore consider that the unusual lactone ring in dregeanin is the C(7):C(1) lactone, involving a [4.3.1] bicyclo bridged nine-membered ring, in which the lactone in the 3-membered bridge is unstable and has a carbonyl absorption at 1787 cm^{-1}. It follows that rohitukin, which shows only the normal absorption of a six-membered lactone, has the alternative C7–C(29) lactone, which involves not a bridged ring, but fused six and seven membered lactone rings. Thus, we propose the structures (**2**) and (**3**) for rohitukin and dregeanin.

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[1] V. P. Gullo, I. Miura, K. Nakanishi, A. F. Cameron, J. D. Connolly, F. D. Duncanson, A. E. Harding, R. McCrindle, and D. A. H. Taylor, *J.C.S. Chem. Comm.*, 1975, 345.

[2] D. A. Okorie and D. A. H. Taylor, *J. Chem. Soc.* (*C*), 1968, 1828.

[3] D. H. Calam and D. A. H. Taylor, *J. Chem. Soc.* (*C*), 1966, 949.