Fragmentation of Some Sesquiterpenoid Lactones Induced by Electron Impact

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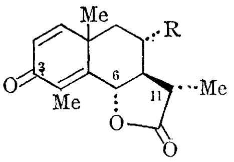
THE mass spectra of a number of sesquiterpenoid lactones[1] have been investigated in detail under high resolution.[2]



(I)

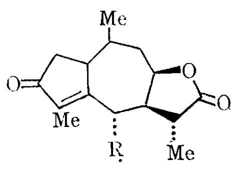
In the santonins (*e.g.*, α-santonin, I, R=H) the molecular ion (*m/e* 246), which is the base peak, loses either methyl (giving *m/e* 231) or carbon monoxide (giving *m/e* 218). The intensity of the former ion is not greatly dependent on the stereochemistry at C-6 or C-11, but that of the latter is considerably greater in the 6-*epi*-compounds having the *cis*-fused lactone ring than in α- and β-santonins in which the lactone is *trans*-fused (see Table). The 3-oxo-group is almost certainly the source of carbon monoxide and must also be lost in the formation of $C_{11}H_{13}^+$ (*m/e* 145) which is much more prominent in the spectra of the 6-*epi*-compounds. Evidently this fragmentation relieves steric strain which from models seems to be greater when the lactone ring has the *cis*-fusion.

TABLE

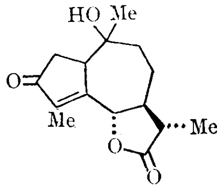
Abundances of fragment ions relative to the molecular ion (M, 100%) *at* 70 ev.

Compound	$M-15$	$M-28$	$M-73$	$M-101$
α-Santonin	30	11	85	19
β-Santonin	30	7	90	16
6-*epi*-α-Santonin	23	20	63	32
6-*epi*-β-Santonin	16	21	60	42

The second most abundant ion in the spectra of the santonins is $C_{12}H_{13}O$ (*m/e* 173). This is shifted to 174 in 2,11-[$^2H_2$]santonin; it evidently corresponds to the loss of the lactone ring together with a proton. A similar fragmentation occurs in 6-deoxygeigerin (II, R=H) and in artemesin (I, R=OH) after the loss of water from the molecular ion to give *m/e* 171, but is much less important in 1,2-dihydrosantonin and 3-deoxytetrahydrosantonin, and does not occur at all in *trans*-2-hydroxycyclohexylacetic acid lactone. Loss of the lactone ring with transfer of either the 11-proton or a proton from the 11-methyl group (in equal probability) gives a less abundant ion at *m/e* 175 in santonin but is particularly favoured in isophotosantonic lactone (III). Geigerin (II, R=OH) undergoes an entirely different reaction involving fission of the seven-membered ring to give $C_9H_{11}O_2^+$ (*m/e* 151, shifted to 153 in 2,2,11-[$^2H_3$]geigerin).

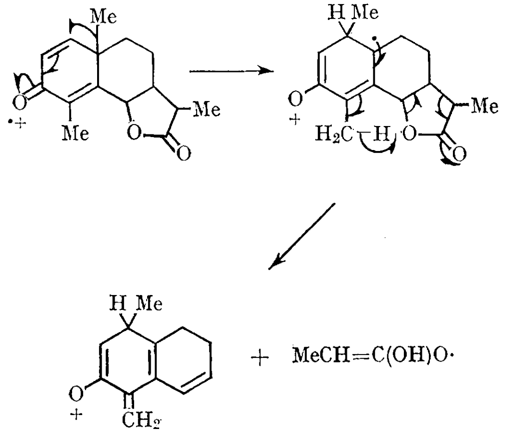


(II)



(III)

In most cases rational mechanisms can be written to account for these fragmentations. The loss of 73 mass units from santonin may involve the migration of the ring-junction methyl:



Few electron impact-induced methyl migrations have been recognized;[3] one of particular relevance to the santonin case occurs in *trans*-Δ^3-10-methyl-2-octalone.

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[1] We are indebted to Dr. J. P. de Villiers for a sample of geigerin and to Professor D. H. R. Barton for the other compounds.

[2] An A.E.I. M.S. 9 double-focusing mass spectrometer was used.

[3] (*a*) F. Komitsky, J. E. Gurst, and C. Djerassi, *J. Amer. Chem. Soc.*, 1965, **87**, 1398; (*b*) P. Brown, C. Djerassi, G. Schroll, H. J. Jakobsen, and S. O. Lawesson, *ibid.*, p. 4559; (*c*) J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson, and G. Schroll, *Chem. Comm.*, 1965, 403.