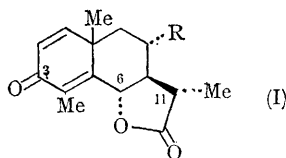


Fragmentation of Some Sesquiterpenoid Lactones Induced by Electron Impact

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THE mass spectra of a number of sesquiterpenoid lactones¹ have been investigated in detail under high resolution.²



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.

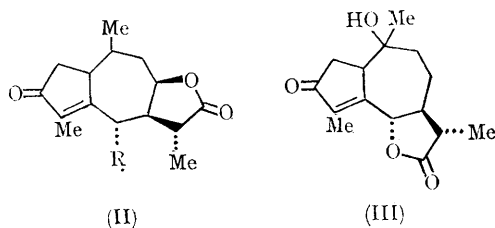
TABLE

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- <i>epi</i> - α -Santonin | 23 | 20 | 63 | 32 |
| 6- <i>epi</i> - 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-deoxy-tetrahydrosantonin, 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 isophotosantonin 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).

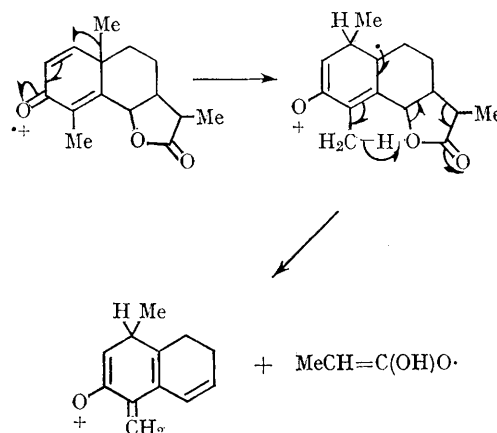
In most cases rational mechanisms can be written to account for these fragmentations. The

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.

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.

(Received, January 18th, 1966; Com. 036.)