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Mass Spectral Study of D-Sesamin from *Phyllarthron comorense*

Krishna C. Joshi, R. K. Bansal, and Pahup Singh
Department of Chemistry, University of Rajasthan,
Jaipur, India

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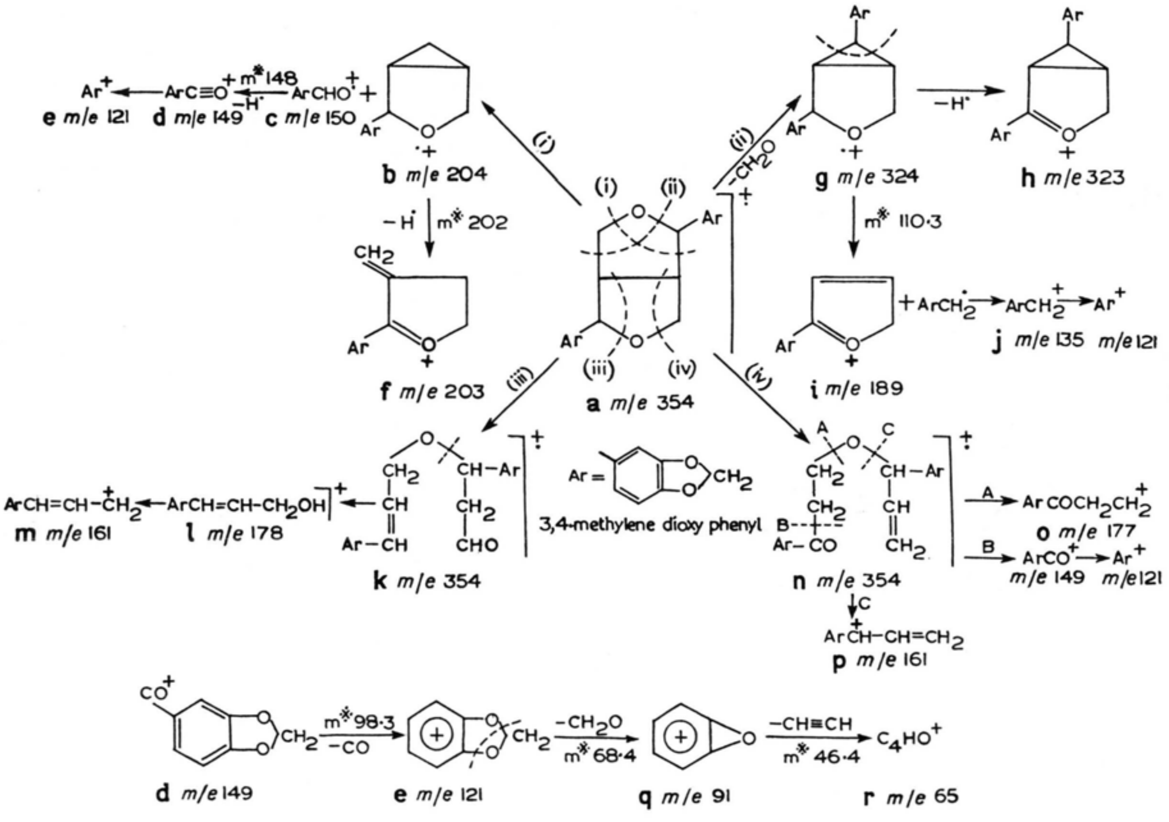
D-Sesamin, *Phyllarthron comorense*, Mass Spectrum

The petroleum ether extract of the heartwood of *Phyllarthron comorense* DC affords D-sesamin along with paulownin, lapachol, dehydrotectol, dehydro-α-lapachone, β-lapachone, tectol and β-sitosterol[1]. We have earlier communicated the mass spectrometric studies of dehydro-α-lapachone[2] and paulownin[3]. The present work deals with the formulation of possible fragmentation schemes in the case of D-sesamin. This compound is a member of 3,7-dioxabicyclo-

Table I. Mass spectral data of D-sesamin[a].

S. No.	*m/e*	Ion composition	Relative intensities
1	354	$C_{20}H_{18}O_6^+$	100
2	324	$C_{19}H_{16}O_5^+$	3.15
3	323	$C_{19}H_{15}O_5^+$	13.7
4	204	$C_{12}H_{12}O_3^+$	17.8
5	203	$C_{12}H_{11}O_3^+$	46.3
6	189	$C_{11}H_9O_3^+$	14.7
7	178	$C_{10}H_{10}O_3^+$	23.1
8	177	$C_{10}H_9O_3^+$	15.7
9	161	$C_{10}H_9O_2^+$	63.1
10	150	$C_8H_6O_3^+$	54.7
11	149	$C_8H_5O_3^+$	75.8
12	135	$C_8H_7O_2^+$	57.8
13	121	$C_7H_5O_2^+$	21.0
14	91	$C_6H_3O^+$	10.0
15	65	C_4HO^+	15.8

[a] The NMR and IR spectra of this compound are consistent with the assigned structure.



MASS SPECTRAL FRAGMENTATION PATTERN OF D- SESAMIN

Requests for reprints should be sent to Prof. K. C. Joshi, University of Rajasthan, Department of Chemistry, *Jaipur* — 302004, India.

(3,3,0)-octane group of lignans. The isolation of D-sesamin has previously been reported by Takahashi *et al.*[4]. However, the present report is the first from genus *Phyllarthron* and from family Bignoniaceae. D-Sesamin consists of two fused tetrahydrofuran rings and follows a fragmentation pattern similar to that of other related lignans reported in literature[5, 6]. The stereochemistry of the substituents in such compounds hardly makes any difference to the cleavage pattern but helps in the determination and confirmation of the carbon skeleton of such molecules.

In the mass spectrum of D-sesamin, molecular ion peak at *m/e* 354 forms the base peak, the intensity of which has been arbitrarily taken as 100%. The various ions and relative intensities have been listed in Table I.

In the present case Ar stands for 3,4-methylenedioxy-phenyl group and the stereochemistry is not implied in the formulae.

The various ions formed in the mass spectral fragmentation of D-sesamin lead to the conclusion that, like paulownin, in this case also molecular ion **a** probably follows four alternate fragmentation patterns indicated by (i), (ii), (iii) and (iv) in the chart.

In scheme (i), the molecular ion **a** leads to the formation of ions **b** of *m/e* 204 and **c** of *m/e* 150. The latter removes one hydrogen thereby forming ion **d** of mass 149, which finally breaks into ion **e** of *m/e* 121. The formation of ion **d** from ion **c** is supported by the appearance of a metastable peak at mass 148. A sharp peak at mass 203 corresponds to the ion **f** which is formed from ion **b** by removal of a hydrogen. The metastable peak at mass 202 is in conformity with this fragmentation.

In scheme (ii), the fragmentation is initiated by the elimination of formaldehyde molecule forming ion **g** at *m/e* 324. A metastable peak at mass 296.6 supports this cleavage. A peak at *m/e* 323, having a comparatively higher abundance than that of ion **g**, may be attributed to ion **h** formed by the elimination of hydrogen from ion **g**. The further fragmentation of ion **g** results in the formation of ion **i** at *m/e* 189. A distinct metastable peak at mass 110.3 indicates that ion **i** is initially accompanied by the formation of free radical $ArCH_2^{\cdot}$ which subsequently changes into ion **j** of *m/e* 135 and finally to the ion Ar^+.

In scheme (iii), no initial fragmentation occurs; instead the molecular ion **a** takes the form **k** which decomposes forming ion **l** of *m/e* 178. The latter finally forms the ion **m** of *m/e* 161.

In scheme (iv) also, no initial elimination takes place but the molecular ion changes to ion **n**. The ion **n** probably undergoes fission at 3 points indicated by A, B and C. The cleavage at point A leads to the formation of ion **o** of *m/e* 177. However, the fission at point B gives rise to the formation of ion at *m/e* 149 which finally changes to ion Ar^+. The cleavage at point C results in the formation of ion **p** at mass 161 which also gives rise to the ion Ar^+ by the elimination of $C_3H_4^+$.

The other ions observed in the mass spectrum indicate that ion **e** (Ar^+) formed by removal of CO molecule from ion **d** undergoes further fragmentation, thereby forming ion **q** at *m/e* 91. The latter finally changes to ion **r** of *m/e* 65. The last two fragmentation processes are supported by the appearance of metastable peaks at appropriate mass units.

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[1] K. C. Joshi, L. Prakash, and P. Singh, Phytochem. **12**, 469 [1973].

[2] K. C. Joshi, L. Prakash, R. K. Bansal, and P. Singh, Z. Naturforsch. **28 c**, 252 [1973].

[3] K. C. Joshi, R. K. Bansal, and P. Singh, Z. Naturforsch. **29 c**, 178 [1974].

[4] K. Takahashi, Y. Tanabe, K. Kobayashi, and T. Nakagawa, J. pharmac. Soc. Japan [Yakugakuzasshi] **83**, 1101 [1963].

[5] A. Pelter, P. Stainton, and M. Barber, J. heterocyclic Chem. **3**, 191 [1966].

[6] A. Pelter, J. chem. Soc. [London] **1967**, 1376.