Mass Spectral Study of Paulownin

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We have earlier reported the isolation of lapachol, dehydrotectol, dehydro-α-lapachone, β-lapachone, tectol, β-sitosterol and paulownin along with d-sesamin from the petroleum ether extract of the heartwood of *Phyllarthron comorense* DC [1]. Paulownin belongs to 3,7-dioxabicyclo-(3,3,0)-octane group of lignans. It was previously isolated and characterised by Takahashi *et al.* [2]. The present report is a second one from a natural source and first from family Bignoniaceae. Paulownin contains two fused tetrahydrofuran rings with a hydroxyl group at ring juncture and follows a fragmentation pattern similar to that of other lignans of such type reported in literature [3, 4]. In such compounds the stereochemistry of the substituents hardly makes difference to the break down pattern, but proves very useful to define and confirm the carbon skeleton of such molecules.

In this case molecular ion peak forms the base peak and its intensity has been arbitrarily taken as 100%. In the present study Ar stands for 3,4-methylene dioxy phenyl group and the stereochemistry is not implied in the formulae. The mass spectral data of paulownin are given in Table. From the ions formed in the mass spectral fragmentation, it may be concluded that molecular ion (**a**) may follow four alternate fragmentation schemes indicated by (i), (ii), (iii) and (iv) in Chart.

Table. Mass spectral data of paulownin [a].

S.No.	*m/e*	Ion composition	Relative intensities
1.	370 (M^+)	$C_{20}H_{18}O_7^+$	100
2.	235	$C_{12}H_{11}O_5^+$	28.9
3.	220	$C_{12}H_{12}O_4^+$	46.3
4.	219	$C_{12}H_{11}O_4^+$	8.8
5.	205	$C_{11}H_9O_4^+$	98.9
6.	191	$C_{11}H_{11}O_3^+$	6.8
7.	177	$C_{10}H_9O_3^+$	5.3
8.	164	$C_9H_8O_3^+$	16.8
9.	161	$C_{10}H_9O_2^+$	30.0
10.	150	$C_8H_6O_3^+$	42.1
11.	149	$C_8H_5O_3^+$	52.6
12.	135	$C_8H_7O_2^+$	52.6
13.	121	$C_7H_5O_2^+$	13.1

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

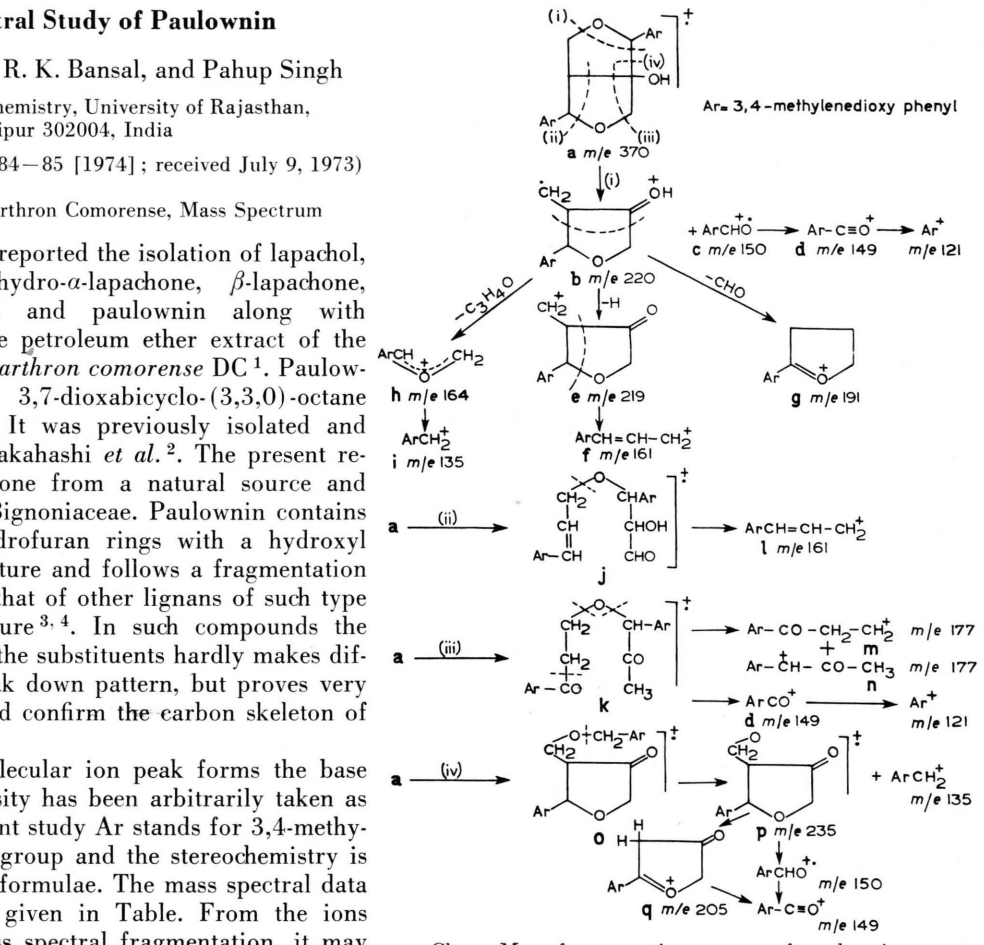

Chart. Mass fragmentation pattern of paulownin

In Scheme (i), molecular ion **a** forms ions **b** of *m/e* 220 and **c** of *m/e* 150. The latter ion changes into ion **d** of *m/e* 149 after losing one hydrogen atom, which subsequently eliminates CO molecule forming an ion of *m/e* 121. The ion **b** breaks down in three ways: the loss of hydrogen atom gives rise to ion **e** of *m/e* 219; the loss of CHO yields the ion **g** having *m/e* 191; while the loss of C_3H_4O unit results in the formation of ion **h** of *m/e* 164 which further decomposes forming benzyl cation **i** of *m/e* 135. The formation of ion **i** clearly established the presence of one Ar group per tetrahydrofuran ring [4]. On the other hand ion **e** gives rise to ion **f** of *m/e* 161.

If scheme (ii) is followed, fragmentation does not occur; instead the molecular ion takes the form **j** which undergoes fission to yield ion **l** of *m/e* 161. Similarly in scheme (iii) the molecular ion, without

undergoing fission, takes the form of ion **k**, which fragments forming ions, **m**, **n** and **d**. The ion **d** decomposes in a manner similar to that in the scheme (i) forming an ion of *m/e* 121.

In scheme (iv), the ion **o** is formed after fission of C – C bond which by elimination of benzyl cation changes into ion **p** of *m/e* 235. The ion **p** follows the usual fragmentation pattern besides forming an ion **q** of *m/e* 205.

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