Mass Spectral Studies of Physcion

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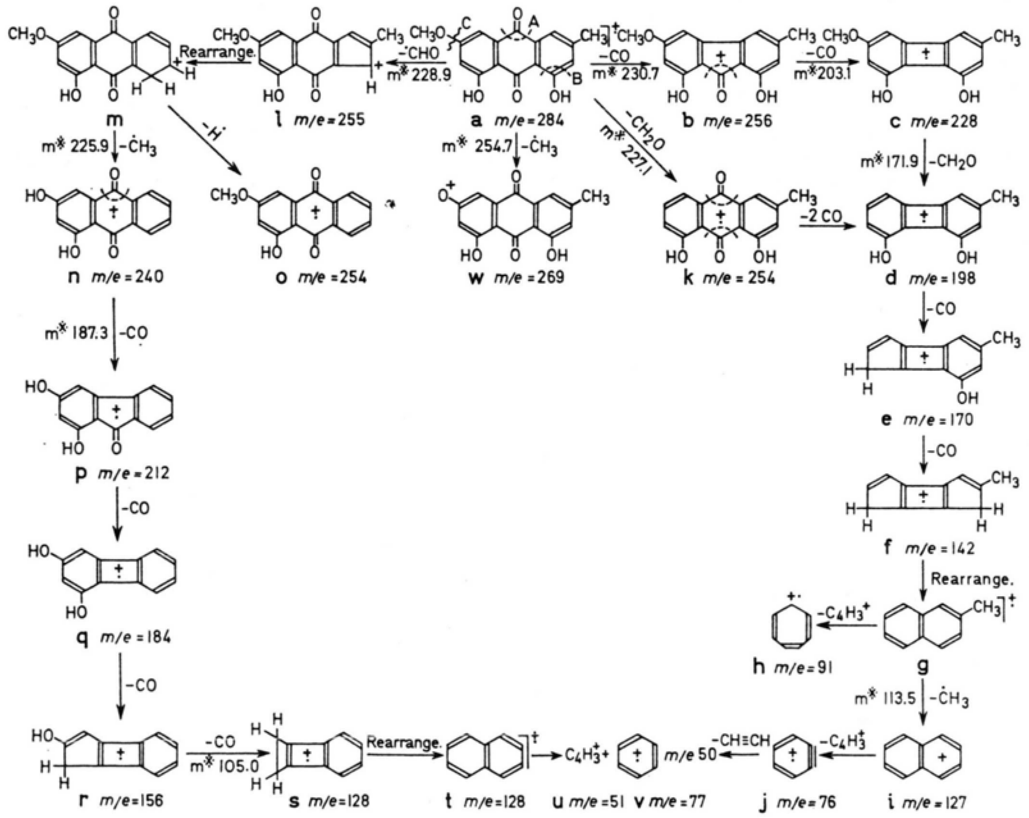
Mass Spectrum, Physcion, *Desmodium pulchellum*

Bansal *et al.* have earlier reported[1] the isolation and identification of a new glycoside, the 1-glycosyl rhamnoside of physcion, from the seeds of *Desmodium pulchellum* Linn. (Leguminosae). The present communication deals with the mass spectral fragmentation studies of the aglycone, physcion, which is 1,8-dihydroxy-6-methoxy-3-methyl anthraquinone. Beynon[2] studied the mass spectrometric fragmentation of a number of hydroxy anthraquinones and postulated that in these cases, preliminary elimination of carbon monoxide or of formyl radical takes place. The peaks observed in the mass spectrum of physcion support these results. In addition, the

Table I. Mass spectral data of physcion *.

S. No.	m/e	Ion composition	Relative intensity
1	284	$C_{16}H_{12}O_5^+$	100
2	269	$C_{15}H_9O_5^+$	10.9
3	256	$C_{15}H_{12}O_4^+$	41.9
4	255	$C_{15}H_{11}O_4^+$	89.1
5	254	$C_{15}H_{10}O_4^+$	36.4
6	240	$C_{14}H_8O_4^+$	5.40
7	228	$C_{14}H_{12}O_3^+$	12.7
8	212	$C_{13}H_8O_3^+$	64.8
9	198	$C_{13}H_{10}O_2^+$	34.5
10	184	$C_{12}H_8O_2^+$	55.6
11	170	$C_{12}H_{10}O^+$	9.09
12	156	$C_{11}H_8O^+$	22.0
13	142	$C_{11}H_{10}^+$	27.3
14	139	—	72.7
15	128	$C_{10}H_8^+$	76.4
16	127	$C_{10}H_7^+$	40.0
17	91	$C_7H_7^+$	18.2
18	77	$C_6H_5^+$	64.8
19	76	$C_6H_4^+$	29.1
20	51	$C_4H_3^+$	76.4
21	50	$C_4H_2^+$	41.8



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* The mass spectra was recorded on a Hitachi Perkin Elmer RMU 6 A spectrometer with direct inlet system. The temperature of the inlet was maintained at 190 °C and an energy of 70 eV was employed. The ionizing current used was of the order of 20 μA.

presence of two other groups, *viz.* $-CH_3$ and $-OCH_3$, gives rise to some other possibilities also. The mass spectral data of physcion are given in Table I. The intensity of molecular ion peak which forms, as expected, the base peak, has been arbitrarily taken as 100%. The relative abundances of other peaks have been calculated accordingly.

The molecular ion may be formed by the removal of one electron from any one of the five oxygen atoms (two hydroxy, two ketonic and one ethereal) thus giving rise to three types of possibilities of fragmentation indicated by A, B and C. In Scheme A, the molecular ion loses successively two molecules carbon monoxide leading to the formation of ions **b** (*m/e* 256) and **c** (*m/e* 228) respectively. This sequence of fragmentation is supported by the appearance of metastable peaks at 230.7 and 203.1 mass units. The ion **c** splits off one molecule of formaldehyde to form ion **d** (*m/e* 198); this type of fragmentation being analogous to that of 2-methoxy naphthaquinone[3]. The elimination of CO molecule from ion **d** results in the formation of ion **e** (*m/e* 170), which further loses one more CO molecule to form ion **f** (*m/e* 142). The latter is stabilised by its rearrangement to ion **g** which is supported by its appreciable abundance. An intense peak is observed at *m/e* 139. Its composition could not be ascertained, and earlier, Beynon has attributed this peak to a highly stabilised doubly charged ion of unknown composition which is commonly found in the mass spectrum of fused ring hydrocarbons[4]. The ion **g** may decompose in two ways – it may split off an ion $C_4H_3^+$ thereby forming tropylium ion at *m/e* 91 or may lose simply a methyl radical to form naphthyl ion **i** at *m/e* 127. The latter gives rise to a benzyne ion **j** (*m/e* 76) which finally results in an ion, *m/e* 50.

In Scheme B, the initial fragmentation occurs at the hydroxyl group, resulting in the elimination of a formyl radical. This process leads to the formation of ion **l** (*m/e* 255), which undergoes rearrangement to form a more stable ion **m**. The higher stability of the latter results from resonance and is confirmed by its high abundance (89.1%). The ion **m** gives rise to ion **n** (*m/e* 240) by simple elimination of a methyl radical. Besides this, the ion **o** (*m/e* 254) forms ion **m** by removal of one hydrogen. The ion **n** follows the usual fragmentation pattern as in the case of hydroxy anthraquinones. The peaks observed at *m/e* 212 and *m/e* 184 may be attributed to the ions **p** and **q** respectively. However, expected metastable peak at 159.7 corresponding to the change of **p** into **q** is not observed. The ion **q** may lose either CO or CHO group, both observed in such cases but the intense peaks observed at *m/e* 156 and *m/e* 128 lead to the conclusion that in this case, the elimination of CO predominates. The ion **s** undergoes rearrangement to form naphthalene ion **t**. The naphthalene ion is highly stable[5] and requires high energy for fragmentation. However, its decomposition leads to the formation of ion $C_4H_3^+$ (*m/e* 51) and phenyl ion at *m/e* 77.

In Scheme C, the preliminary fragmentation takes place at the ethereal linkage. In this case the molecular ion may either split off a formaldehyde molecule giving rise to the formation of ion **k** corresponding to ion $M\text{-}CH_2O$ or it may simply lose a methyl radical to form ion $M\text{-}CH_3$ at 269. This type of fragmentation occurs in case of 2-methoxy-1,4-naphthaquinone also[3]. Moreover, the formation of these ions is confirmed by the appearance of appropriate metastable peaks. The ion **k** of *m/e* 254 finally changes to ion **d** by splitting off two CO molecules.

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