Asian Journal of Chemistry Vol. 4. No. 4 (1992), 927–929

NOTES

Mass Spectral Studies of Some 3-Benzyloxy Flavones

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Mass spectral fragmentation pattern of four 3-benzyloxy flavones has been discussed.

Electron impact mass spectrometry serves as a valuable aid in determining the structure of flavonoids. The general rules for interpretation of molecular formula, type and number of substitutions in the three rings of the flavonoid skeleton and in some cases the exact location of these substitutions have been treated extensively[1–3]. In addition to the molecular ion, perhaps the most useful fragmentations in terms of flavonoid identification are those which involve cleavage of intact A and B ring fragments. Such ions are designated as A_1, A_2 and B_1 and B_2...etc. respectively. Some of these ions are derived by retro-Diels-Alder (RDA) processes. Two common fragmentations of flavonoids are those designated as pathway-I and pathway-II. Pathway-I corresponds to a retro-Diels-Alder cleavage which commonly produces two different ions generally represented as $A_1^{+\cdot}$ and $B_1^{+\cdot}$ whereas pathway-II yields predominantly a single charged species B_2^+ ($C_6H_5C{=}\overset{+}{O}$).

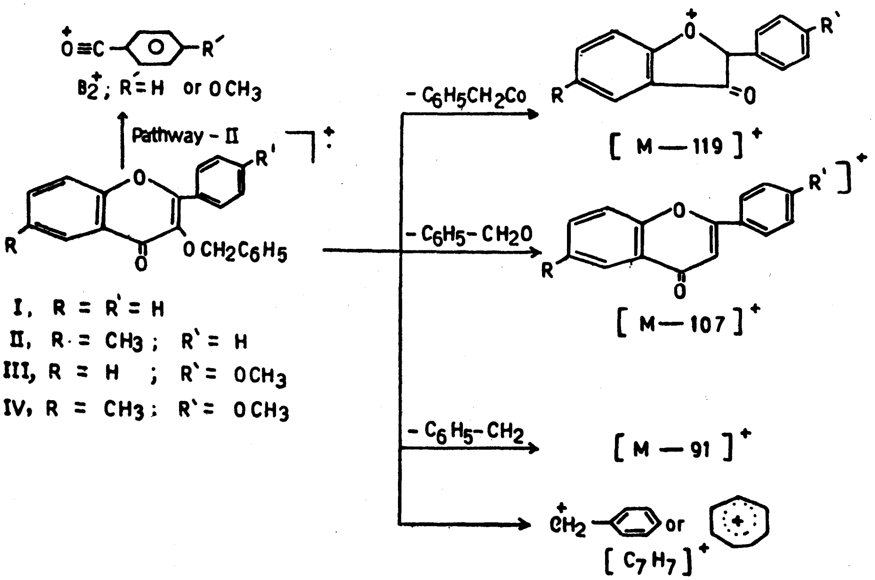
The data available for 3-benzyloxy flavones (I to IV) indicate that molecular ion loses radical ($C_6H_5CH_2CO$) to form stable cation $(M-119)^+$. Invariably the loss of this radical is especially favoured sufficiently sometimes to lead to the base peak of spectrum. The process which leads to $(M-C_6H_5CH_2CO)^+$ ion is a major fragmentation pathway for 3-benzyloxy flavones leading to the formation of an internal five membered ring. The molecular ion by concerted loss of CO and a benzyl radical possibly as a $C_6H_5CH_2CO$ may produce $[M-119]^+$. The other important fragmentation pathway of compounds III and IV is the loss of benzyl radical to give $[M-91]^+$ ion and loss of benzyloxy radical in compound I and II produces $[M-107]^+$ ion. The other diagnostic fragments from 3–benzyloxy flavones are the pathway-II B-ring ion B_2^+ (C_6H_5–$C_6{\equiv}\overset{+}{O}$). Further the benzyl fragment is also prominent in the fragmentation studies of such compounds and this ion $[C_7H_7]^+$ may be associated with its rearrangement to a tropylium structure (Scheme I). The above fragments with their relative intensities have been recorded in Table 1.

TABLE 1

MS IONS FROM 3-BENZYLOXY FLAVONES m/z VALUES (RELATIVE INTENSITIES)

Compd.	M^+	$[M-C_6H_5CH_2CO]^+$ $[M-119]^+$	$[M-C_6H_5CH_2O]^+$ $[M-107]^+$	$[M-C_6H_5CH_2]^+$ $[M-91]^+$	B-ring Ion B_2^+	$[C_7H_7]^+$
I	328(50)	209(50)	225(25)	—	105(25)	91(100)
II	342(75)	223(100)	236(40)	—	105(20)	91(90)
III	358(30)	239(100)	—	267(25)	135(10)	91(25)
IV	372(40)	253(100)	—	281(20)	135(10)	91(15)

SCHEME I



Melting points were taken in open capillary tubes and are uncorrected. Purity of the products was determined by TLC on silica gel plates using C_6H_6-ethylacetate (95.5; v/v) as irrigant.

Flavonols used for this reaction were prepared by literature methods[4].

General Method for 3-Benzyloxy Flavones (I to IV)

A mixture of flavonol (0.01 mole), benzylchloride (0.01 mole) and anhydrous K_2CO_3 (0.02 mole) in acetone (100 ml) was refluxed until it gave negative test with alcoholic ferric chloride (10–15 hrs). After the completion of the reaction, the solid K_2CO_3 was filtered off and washed with boiling acetone (3×50 ml). The washings were mixed with the filterate and the solvent was distilled off. The residue was triturated with ether and the separated solid was filtered and crystallised from ethanol to afford analytical samples.

Compound I :—m.pt. 87–88°C yellow needles, yield 62%, Found C, 80.47 H, 4.85 $C_{22}H_{16}O$ (328.3) requires C, 80.47; H, 4.91%.

Compound II : —m.pt. 99–100°C, yellow needles, yield 69%, Found C, 77.30; H, 5.01 $C_{22}H_{18}O_4$ (358.4) requires C, 77.08; H, 5.06%.

Compound III :—m.pt. 122–123°C, light orange needles which darkens on exposure to air without any change in m.pt., yield 55%, Found C, 80.43; H, 5.30 $C_{23}H_{18}O_3$ (342.4) requires C, 80.68 H, 5.29%.

Compound IV :—m.pt. 113–114°C, yellow needles, yield 54%, Found C, 77.11; H, 5.43 $C_{24}H_{20}O_4$ (372.4) requires C, 77.40; H, 5.41%.

ACKNOWLEDGEMENTS

The authors are grateful to the Head, Department of Chemistry, University College of Science for providing departmental facilities and Dr. L. Bauer, Professor of Medicinal Chemistry, Chicago, Illinois, U.S.A. for elemental and mass spectral data. Financial assistance from CSIR (RBB) and UGC (AA) New Delhi as JRF and Project Assistant respectively is also thankfully acknowledged.

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(*Received*: 4 December 1990; *Aecepted*: 1 July 1991) AJC–373