Tetrahedron Letters No.5, pp. 471-473, 1967. Pergamon Press Ltd. Printed in Great Britain.

THE STRUCTURE OF MARMIN

Mrs. A. Chatterjee, C. P. Dutta and Miss S. Bhattacharyya
University College of Science, Calcutta-9, India.

H. E. Audier and B. C. Das
Institut de Chimie des Substances Naturelles, C.N.R.S.,
Gif-sur-Yvette (Essonne), France.

(Received 28 November 1966)

Marmin, m.p. 123-124°, $[\alpha]_D + 25°$ (EtOH), a new coumarin, was isolated from the trunk bark of Aegle marmelos Correā (Rutaceae) and a structure was proposed (1) for this compound on the basis of the molecular formula $C_{19}H_{26}O_5$. Mass spectrometric and nuclear magnetic resonance studies show that the correct molecular formula is $C_{19}H_{24}O_5$ and that the chemical structure of marmin should be revised to (I).

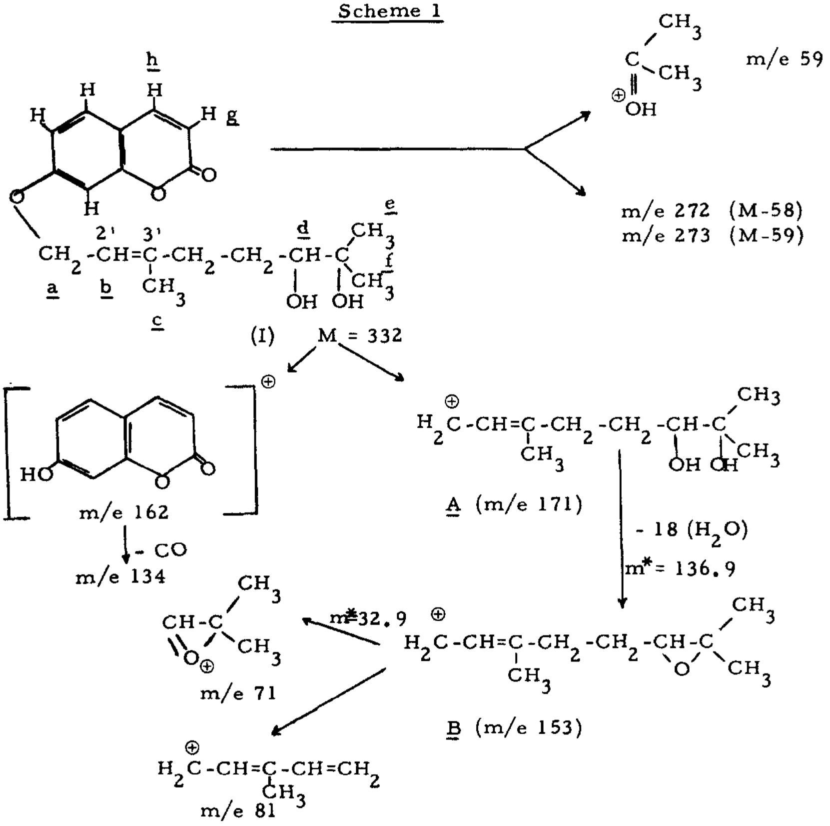
The U.V. absorption spectrum of marmin shows a maximum at 324 mμ (log ε 4.23) similar to that observed for umbelliferone methyl ether and it is not affected by addition of base indicating the absence of a free phenolic hydroxyl group. The I.R. spectrum has bands at 3500 (hydroxyl), 1720 (coumarin lactone ring), and 1615 cm^{-1} (aromatic ring).

The mass spectrum (2) of marmin exhibits the molecular ion peak at m/e 332 corresponding to the formula $C_{19}H_{24}O_5$, which was confirmed by accurate mass measurement (found : 332.1619 ; calc. : 332.1623). Upon deuteration this is shifted to m/e 334 indicating the presence of two hydroxyl groups in marmin. The significant ion fragments with their probable structural assignments are shown in Scheme 1. The base peak in the spectrum is observed at m/e 162 (found: 162.0315 ; calc. for $C_9H_6O_3$: 162.0316) which corresponds to the molecular composition of umbelliferone. This together with the presence of a peak at m/e 171 (ion A ; found: 171.1384 ; calc. for $C_{10}H_{19}O_2$: 171.1385) suggests that marmin is an ether of umbelliferone having a 10-carbon ether chain, which should contain two hydroxyl groups. This is supported by the fact that the peak at m/e 171 is shifted to m/e 173 when exchanged with deuterium. Furthermore, the composition of the fragment A (m/e 171 ; $C_{10}H_{19}O_2$) points to the presence of a double bond equivalent in the C_{10}-ether chain. Loss of a molecule of water from A leads to the ion B (m/e 153) which undergoes further fragmentation to give a peak at m/e 71. An intense peak is also observed at m/e 81. In agreement with the mechanism suggested in Scheme 1, these peaks at m/e 153, 81 and 71 remain unshifted upon deuterium exchange. A peak at m/e 59, shifted to m/e 60 upon deuteration indicates the presence of a terminal hydroxy-isopropyl group in marmin.

Isolation of acetone and levulinic acid from the periodic-acid as well as chromic-acid(1) oxidation products of marmin clearly indicates the presence of (i) a terminal hydroxy-isopropyl group, (ii) a α-glycol linkage and (iii) a double bond (3) between 2' and 3' carbon atoms of the ether side-chain.

All the above results are in agreement with the structure (I) for marmin.

Scheme 1



Final confirmation of the structure (I) of marmin rests on the analysis of its N.M.R. spectrum (60 Mc/sec. in $CDCl_3$). The two protons (a) of the methylene attached to the ether oxygen appear at 5.40 τ (2H) as a doublet and the olefinic proton (b) at 4.50τ(1H) as a broad triplet. The signal at 8.22 τ (3H ; broad singlet) is ascribed to the methyl group (c) on a double bond. The tertiary hydrogen, d, occurs as a quartet around 6.65 τ and the two terminal methyl groups (e, f) absorb at 8.80 (3H) and 8.84 (3H). A signal at 7.58 τ is assigned to the hydroxyl groups since it disappears on the addition of deuterium oxide to the solution. The two olefinic protons, g and h, appear at 3.78 and 2.38 τ (J = 9.5 cps), respectively, as expected of coumarin compounds (4). The signals for the three aromatic protons are observed at 3.18 (2H ; multiplet) and 2.7 τ (1H ; doublet).

Acknowledgement

We would like to thank Professor E. Lederer for his interest in this work. Partial support by means of a grant from the Indian Council of Medical Research is gratefully acknowledged.

References

1. A. Chatterjee and A. Battacharya, J. Chem. Soc., 1922 (1959).
2. All mass spectral measurements were made with A.E.I. MS9 mass spectrometer operating at 70 e.v.
3. A. Chatterjee and S. Ghosh Majumder, Analytical Chemistry, 28, 878 (1956).
4. High resolution N.M.R. spectra Catalog, spectrum No.225, Varian Associates, Palo Alto, California, (1962).