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NATURAL COUMARINS. XIII. THE STRUCTURE OF MAJURIN, A NEW CONSTITUENT OF AMMI MAJUS L. FRUITS

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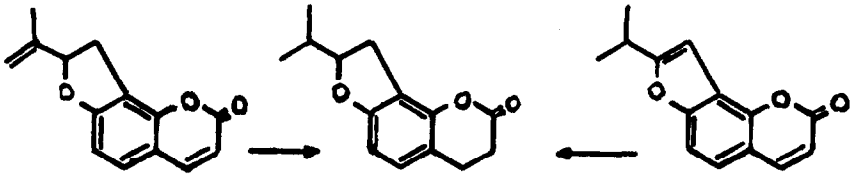
A new coumarin, to be named majurin, has been isolated from Ammi majus L. fruits and was shown to be different from the hitherto known[1] linear furocoumarins of this source in having a skeleton with angular disposition. Majurin, m.p. 95-96°, was isolated in about 0.0003 % yield from the glycosidic coumarin fraction (after acid hydrolysis) of A. majus L. fruits, as a minor companion of marmesin[2], by preparative-layer chromatography on silica gel. The compound has the composition $C_{14}H_{12}O_3$ (mol. wt. 228.0786), gives the usual coumarin reactions and is evidently nonhydroxylic. It exhibits UV absorption characteristics (λ_{max} 253 and 328 mu, log ε = 3.70 and 4.15, respectively) concordant with a dihydrofurocoumarin constitution.[2]

The NMR spectrum contained a pair of doublets at δ7.62 and 6.19 (for the α-pyrone protons at C-4 and C-3, respectively, $J_{3,4}$= 10 c/s) in addition to two other doublets at δ7.27 and 6.75 due to ortho protons (J=8 c/s) in a 1,2,3,4-tetrasubstituted benzene system. The presence of a third ring fused to the aromatic ring in an angular (5,6- or 7,8-) position is thus indicated and its nature as a dihydrofuran carrying a side chain, presumably on the α carbon atom, was evidenced by an octet at δ3.32 (for the β CH_2) and a triplet at δ5.37 (for the α CH). The shape of the latter signal (absence of further splitting) suggests that there is no proton on the first carbon of the side chain which is evidently an isopropenyl group (demonstrated by a methyl group singlet at δ1.76 and a CH_2 signal at δ5.03) attached to the α carbon of the dihydrofuran system. A consideration of the positions of the two benzenoid proton signals

suggests that one proton (that giving the upfield signal at δ6.75) must be adjacent to an oxygen substituent while the other (that giving the signal at δ7.27) is not, in accordance with the observations of Bredenberg and Shoolery[3] for related systems. Accordingly, only two of the four possible isomeric structures of majurin appear most likely; of these structure I is strongly favoured on biogenetic grounds since it embodies an umbelliferone residue as do all the other coumarins of A. majus L.



I II III

The mass spectrum of majurin exhibits fragmentations which are concordant with structure I and include losses of CH_3, CO and C_4H_5 from M^+ in addition to two CO expulsions from the M^+-CH_3 ion. Structure I received final support by catalytic hydrogenation of majurin which afforded the same product (hexahydrooroselone,[4] II) as did dihydrooroselone (III). Evidently, majurin occurs naturally as a glycoside in which the sugar is likely bound to the phenolic hydroxyl of the corresponding open coumarinic acid.

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