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Reaction of Furanocoumarins with Aluminium Chloride in Benzene*

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The reaction of AlCl_3 and benzene on the naturally occurring linear furanocoumarin chalepensisin (II) is shown to give crystalline benzene addition product, $\text{C}_{24}\text{H}_{32}\text{O}_2$, m.p. 191° . On the basis of NMR and mass spectra it has been formulated as (III). Similar benzene addition products from psoralen and angelicin earlier assigned the structures IV and V respectively [*Proc. Indian Acad. Sci.*, 16A (1942), 151] have now been shown on the basis of NMR and mass spectra to have the structures (VI) and (VII) respectively.

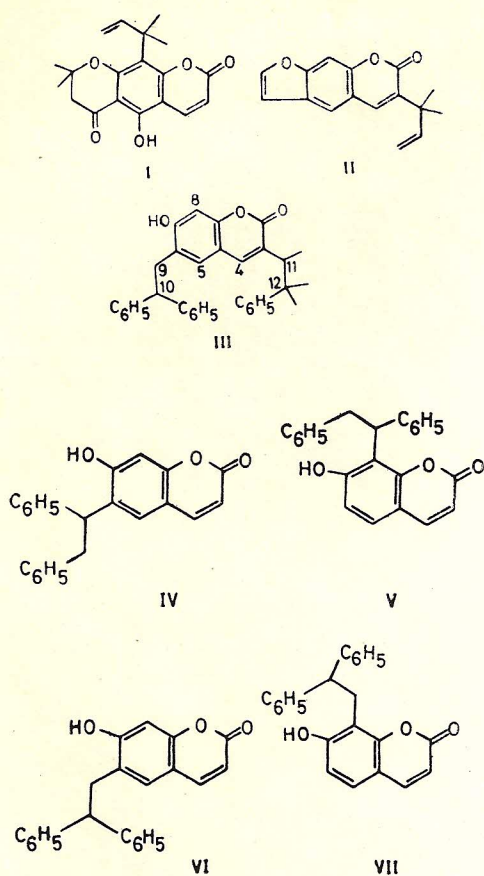
THE 1,1-dimethylallyl group of clausenidin (I) could be cleaved in a reverse Friedel-Crafts reaction using AlCl_3 in benzene^{1,2}. The furano-

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coumarin chalepensisin³ (II) isolated from the roots of *Clausena indica* Oliv.⁴ when refluxed with AlCl_3 and benzene gave a crystalline product, m.p. 191° .

The same compound was obtained from xylostenin (\equiv chalepensisin⁴) by refluxing in dry benzene in presence of HCl gas and AlCl_3 and was reported to have M^+ 370 and λ_{max} 340 nm ($\log \epsilon$ 4.02)⁵. The reaction product obtained by us was soluble in alkali, showed an intense blue fluorescence and exhibited in the UV λ_{max} 250, 260 and 340 nm ($\log \epsilon$ 3.76, 3.71 and 4.26). It analysed for the formula $\text{C}_{24}\text{H}_{32}\text{O}_2$ and showed molecular ion peak at m/e 488 of low intensity. Its NMR spectrum (CD_3COCD_3 ; TMS = O) showed the following signals: secondary methyl δ 0.92 (C_{11}CH_3 ; d ; $J = 7.5$ Hz), tertiary methyls 1.26 (C_{12}CH_3 ; 6H; s), benzylic methylenes 3.45 ($\text{C}_9\text{Ar-CH}_2$; d ; $J = 7.5$ Hz), 3.5 ($\text{C}_{11}\text{Ar-CH}$; q ; $J = 7.5$ Hz), 4.55 ($\text{C}_{10}\text{Ar-CH}$; t ; $J = 7.6$ Hz); aromatic protons δ 6.75-7.4 (18H; m) and phenolic OH 9.4 (1H, s). On the basis of the NMR spectrum and the mass-spectral fragmentation (Chart 1), the reaction product has been formulated as (III).

The tertiary fragment (a) cleaves readily giving rise to the base peak (b) at m/e 369. This being



the most intense peak in the mass spectrum, M-118 was probably mistaken for the molecular ion peak⁵.

Krishnaswamy and Seshadri⁶ studied the reaction of AlCl_3 and benzene on the linear and angular furanocoumarins, viz. psoralen and angelicin and formulated the benzene addition products as (IV) and (V) respectively. However, these products are consistent with structures (VI) and (VII). NMR spectra of both the compounds show two sets of doublets around δ 6.0, 7.4 ($J = 9$ Hz) due to C_3 , C_4 coumarin protons and the benzylic methylene protons at 3.55 (2H; d ; $J = 8$ Hz) and 4.6 (1H; t ; $J = 7.5$ Hz) but the chemical shifts are not useful in distinguishing between the two alternative formulae. However, the mass spectra of both the compounds clearly favour the structures (VI) and (VII). They show the molecular ion peak M^+ at m/e 342 (25 and 2% respectively) and the base peak at m/e 167 which should be due to the diphenylmethyl ion (c)⁷. The other prominent peaks are m/e 175, due to the tropylium ion $\text{C}_{10}\text{H}_7\text{O}_3^+$ and m/e 147 obtained from m/e 175 by the loss of carbonyl⁸.

The formation of VI and VII from psoralen and angelicin possibly involves the opening of the furan ring to give an intermediate acetylene which adds benzene to give the diphenylethane deri-

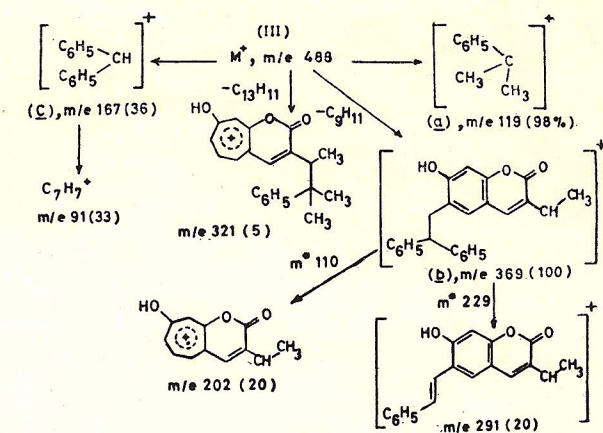
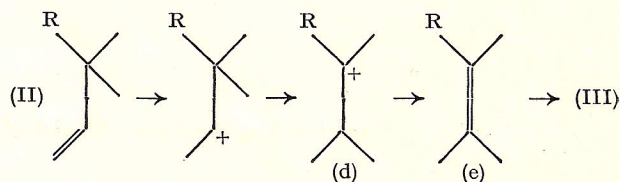


Chart 1 — Mass spectral fragmentation pattern of compound (III)

vatives⁹. In the case of chalepensis II to give III, apart from the addition of benzene by opening of the furan ring, there is also a rearrangement of the 1,1-dimethylallyl group preceding the benzene addition. The mechanism postulated is an initial methyl shift to form the more stable tertiary carbonium ion (d), formation of an ethylene (e) and addition of benzene to the double bond to give (III)¹⁰.



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