Lubimin: A Phytoalexin of Several *Solanaceae*. Structure Revision and Biogenetic Relationships[†]

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Summary A new structure proposed for the phytoalexin, lubimin, correlates it biogenetically with other bicyclic sesquiterpenes of the *Solanaceae*.

Lubimin, one of the phytoalexins[3] produced when potatoes (*Solanum tuberosum*) are subjected to certain stresses, was assigned structure (**1**) by Metlitskii and his co-workers.[4] We recently isolated the same compound from the fruit of the egg-plant (*Solanum melongena*) inoculated with *Monilinia fructicola* or other fungi, and also from *Datura stramonium* inoculated similarly. The substance, $[\alpha]_D^{32} + 39$ (1% in EtOH), was indistinguishable by all used criteria, including ^1H n.m.r., i.r. and mass spectra, from lubimin, prepared from potatoes as described in the literature[4] (except that *M. fructicola* was used as inducer and t.l.c. for isolation.) The ^{13}C n.m.r. spectrum (in $CDCl_3$), however, showed that structure (**1**) cannot be correct, since it would account for only one quaternary C-atom (that of the isopropenyl residue at 147·3 p.p.m.). Off-resonance decoupling experiments

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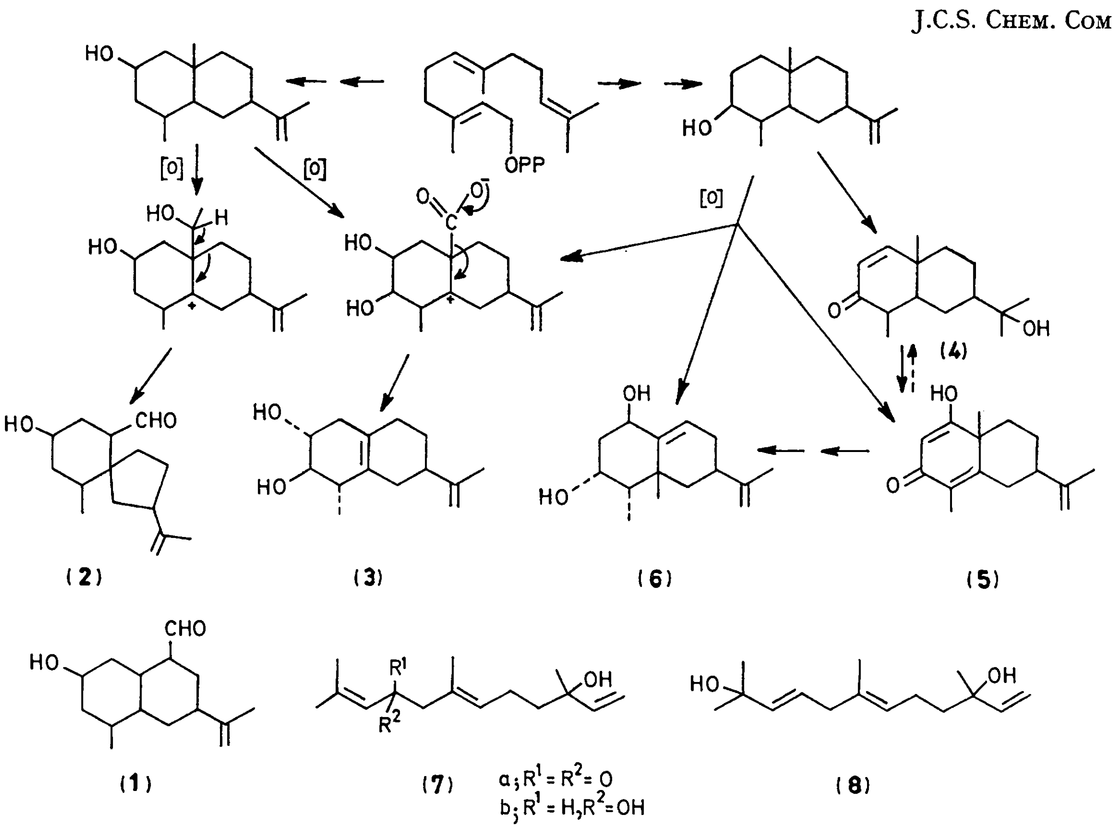
[†] For other work in this field see refs. 1 and 2.



Scheme

showed that the molecule comprises a second quaternary C (46·9 p.p.m.), five –CH$_2$– groups (25·9, 32·6, 33·3, 40·3 and 41·8 p.p.m.), five carbons which can be assigned respectively to –CHO (204·9), –CH(OH)– (69·3), secondary Me- (16·4), Me- (21·2) and =CH$_2$ (108·8 p.p.m.) of the isopropenyl group and three other tertiary C-atoms (41·8, 47·4 and 58·4 p.p.m.) Also, ^{1}H n.m.r. decoupling studies support the presence of the part structure $-CH_2-CH(OH)-CH_2-CH(CHO)-\overset{|}{\underset{|}{C}}-$. A precise mass determination gave the formulation of lubimin as $C_{15}H_{24}O_2$ and the molecule is consequently bicyclic. These data can be accommodated formally by a number of structures but only structure (**2**) incorporates a known[5] sesquiterpenoidal carbon skeleton and is biogenetically plausible. Structure (**2**) is consistent with the fact that in potatoes, rishitin[6] (**3**) is induced at the same time as lubimin (Scheme) and also consistent with this proposal is the induction of a second compound in the inoculated egg-plants, which can be assigned structure (**4**) on the basis of its spectroscopic properties [λ_{max} (EtOH) 227 nm (log ϵ 3·93); ν_{max} (liq.) 3455, 3030, 1667, and 756 cm^{-1}; δ (^{1}H) 1·13 (d, *J* 7·5 Hz, *Me*-CH), 1·14 (s, *Me*–C–), 1·23 (s, *Me*$_2$C–O–), 2·39 (m, Me–CH–), 5·86 and 6·77 (AB pair, *J* 10 Hz, –CO–CH=CH–C–); δ (^{13}C) 13·4, 20·8, 27·2, 27·6 (Me's), 22·4, 26·1, 40·0 (CH$_2$'s), 44·5, 45·3, 49·1 (CH's), 36·2, 72·6 (quaternary C's), 125·9, 160·9 (=CH's), and 204·0 p.p.m. (C=O)]. The compound, which has no significant antifungal activity, is very similar in structure to 1-keto-α-cyperone (**5**) from tobacco.[7] This, in turn, has the oxygenation pattern of capsidiol (**6**), the *Capsicum frutescens* phytoalexin,[8] which presumably is formed by methyl migration. Thus, the biogenesis of these solanaceous compounds can be described tentatively by a scheme similar to that proposed by Andersen[9] for the sesquiterpenes of vetiver oil.¶

Three other compounds isolated from the *M.fructicola*-treated egg-plant, and not detected in water-treated controls, were (**7a**) (identical with the 9-oxonerolidol recently reported by Hiroi[10] from camphor leaf oil), its 9-hydroxy analogue (**7b**) and the allyl isomer (**8**).

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¶ Since the submission of this manuscript we have learned, through the courtesy of Dr. R. F. Curtis, ARC Food Research Institute, Norwich, that a report on two other vetispiranes from potatoes was submitted for publication in Tetrahedron Letters by D. T. Cox *et al.* on the same date.