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THE STRUCTURE OF ABSCISIN II

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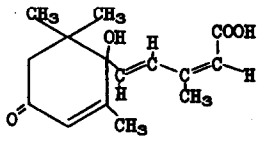
The isolation and characterization of abscisin II, an abscission-accelerating plant hormone from young fruit of cotton (Gossypium hirsutum L.), have been described (1,2). We now wish to propose the biogenetically reasonable structure A for this substance.



A

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The very small amount (nine milligrams) of crystalline material available has limited our investigation to the measurement and interpretation of elemental analysis, mass spectrum and infrared (IR), ultraviolet (UV) and nuclear magnetic resonance (NMR) spectra.

Combustion analysis of one milligram of abscisin II showed 68.76 percent carbon and 7.96 percent hydrogen. These data taken together with the mass spectral parent peak at 264 mass units strongly indicate the molecular formula $C_{15}H_{20}O_4$ even though the analytical data do not agree with the calculated percentages (C:68.16%;H:7.63%) within the usually accepted limits.

The major features of the previously published (1) IR spectrum of abscisin II (KBr pellet) include a rather sharp band at 3405 cm^{-1} typical of an alcoholic hydroxyl in addition to the broad band ranging down to 2300 cm^{-1} characteristic of a carboxylic acid. The presence of the latter functional group is confirmed by the solubility of abscisin II in aqueous sodium bicarbonate.

The carbonyl and double bond stretching region is complex; if the strong peak at 1650 cm^{-1} is taken to represent a conjugated keto group then the other three bands (1674, 1623 and 1600 cm^{-1}) are at positions characteristic of sorbic acid and its alkyl derivatives.* The relatively strong band at 978 cm^{-1} is characteristic of a <u>trans</u>-disubstituted double bond.

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* In particular, hydroxyisophorone absorbs at 1652 cm^{-1} and <u>cis</u>, <u>trans</u>-β-methylsorbic acid at 1686, 1633 and 1602 cm^{-1}.

In agreement with the assumption made above, addition of the UV absorption curves of isophorone (λ_{max}^{MeOH} 236 mμ; ε = 12,600) and cis,trans-β-methylsorbic acid (3,4) (λ_{max}^{MeOH} 255 mμ; ε = 17,600) leads to a composite having λ_{max} 244 mμ (ε = 24,800) in good agreement with the maximum of abscisin II at 246 mμ (ε = 25,200) in methanol.

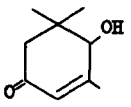
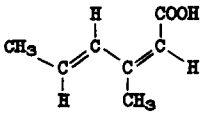
The 60 mc. NMR spectrum (see Table 1) contains two singlets corresponding to two methyl groups on saturated carbon, two slightly broadened singlets corresponding to vinylic methyl groups, the two stronger peaks of a non-equivalence quartet (verified in a 100 mc. spectrum) whose area and field position suggest a methylene group adjacent to the carbonyl, and finally, two slightly broadened singlets and a pair of doublets with a coupling constant of 16 cycles per second (c.p.s.), indicating a total of four vinyl protons. The chemical shifts of the two singlet vinyl protons are consistent with placement α or γ (but not β or δ) to a carbonyl group, and the coupling constant of the doublets is typical for protons trans across a double bond.

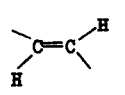
These spectral data indicate the presence in abscisin II of the structural units B-E and, since no NMR signal appears in the region associated with protons bound to carbon bearing oxygen, F is present. There remain three carbon atoms to be accounted for, two of which are methyl groups; therefore, structural unit G is present. Now, from the molecular formula and the fact that only five instances of unsaturation have been accounted for, it follows that abscisin II must be monocyclic.

TABLE 1

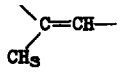
NMR Peaks in p.p.m. Downfield from Tetramethylsilane

(A = relative area)

Abscisin II		
1.10 (A = 3)	1.04	
1.17 (A = 3)	1.09	
1.99 (A = 3)		2.00
2.10 (A = 3)	2.08	
	(2.19)	
2.41	2.28	
2.47	2.36	
	(2.62)	
5.79 (A = 1)		5.60
5.98 (A = 1)	5.84	
6.17 (A = 1)		6.16
doublet, J = 16 c.p.s.		multiplet
7.81 (A = 1)		7.57
doublet, J = 16 c.p.s.		doublet, J = 16 c.p.s.

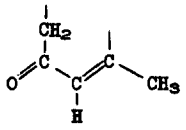


B



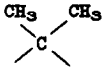
C

D



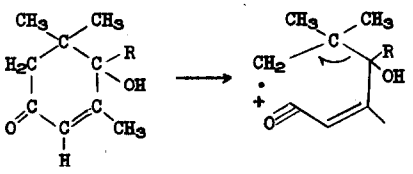
E

F

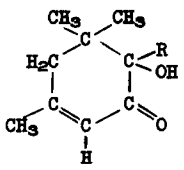


G

Units B-D clearly must be used to form the sorbic acid side chain and only two arrangements (H and I) of the remaining pieces are permitted by the NMR data.



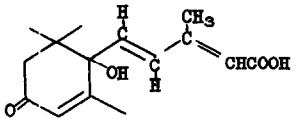
H



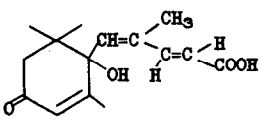
I

Of these, H is preferred on the basis of a strong peak at 208 mass units (P-56) in the mass spectrum of abscisin II as would be expected (5) from the loss of isobutylene from H but not from I.

Addition of pieces B-D can only be accomplished in two ways (J and K) which are consistent with the NMR splitting pattern:



J



K

Since abscisin II is the product of a higher plant the isoprenoid structure J is the more likely.

Finally, comparison of the chemical shifts for the methyl group β and the proton γ to the carboxyl group of cis,trans-β-methyl sorbic acid (Table 1) with those of the trans,trans acid (4) at 2.29τ (A = 3) and 6.17 (multiplet containing both γ and δ protons) demonstrates the cis-configuration of the α,β-double bond and completes the proof of the structure and stereochemistry of abscisin II as pictured in structure A.

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