Phaseic Acid, a Putative Relative of Abscisic Acid, from Seed of *Phaseolus multiflorus*

By J. MACMILLAN* and R. J. PRYCE
(*The Department of Organic Chemistry, The University, Bristol*)

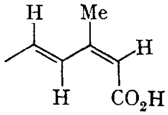
WE report the isolation of a monocarboxylic acid $C_{15}H_{20}O_5$ (Found *m/e* 280·132) from immature seed of *Phaseolus multiflorus*; this acid which we name phaseic acid is identical to the uncharacterised acid, m.p. 207—209°, previously obtained from the same source by MacMillan *et al.*[1] With the limited amount of phaseic acid available (6 mg. from 25 kg. seed), present information on the structure is derived mainly from spectroscopic evidence which indicates the presence of the groupings (I—V).†

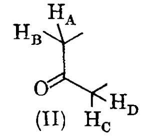
The β-methyl-2-*cis*-4-*trans*-dienoic acid grouping (I) is indicated by (i) the ultraviolet spectrum [λ_{max} (MeOH) 258 mμ (ϵ, 14,500)]; (ii) the infrared spectrum [ν_{max} (Nujol) 1684, 1670sh, 1637, and 1610 cm.$^{-1}$]; (iii) the n.m.r. spectrum (τ in $CDCl_3$) of the methyl ester which showed signals assigned to the β-methyl (8·04, d, J = 1·5 c./sec.), the α-proton (4·28, q, J = 1·5 c./sec.) and to the γ- and δ-protons (3·82 and 1·89, J_{AB} = 16 c./sec.), and (iv) the mass spectrum of phaseic acid and its methyl ester which showed peaks at *m/e* 111 and

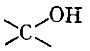
---

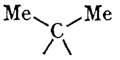
† Although evidence is presented mainly for the acid, corroborative data have been obtained for the monomethyl ester, $C_{16}H_{22}O_5$, m.p. 155—158°.

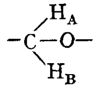
125 respectively due to the rearrangement ions (VII; R = H and Me).[2,3]

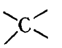

(I)

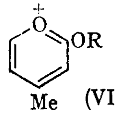

(II)

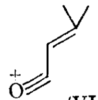

(III)

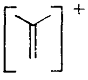

(IV)

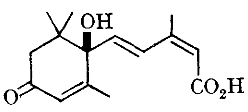

(V)

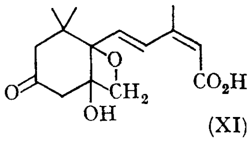

(VI)

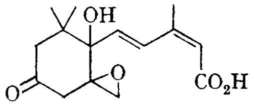

(VII)


(VIII)


(IX)


(X)


(XI)


(XII)

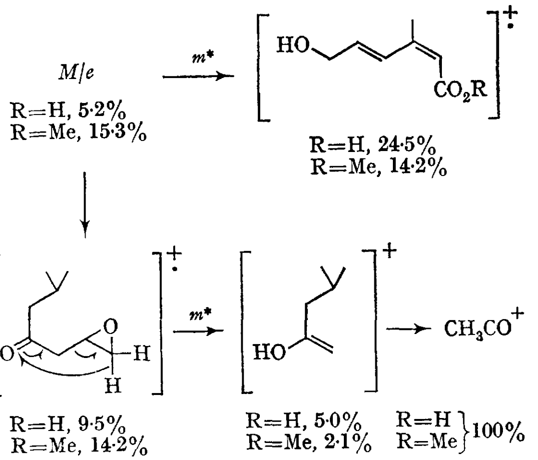
The n.m.r. spectrum [τ in $(CD_3)_2CO$] of the acid contained two overlapping AB-quartets (7·25, 7·64, 7·33, 7·71, J_{AB} = 18 c./sec. in both cases) which indicated the grouping (II); the carbonyl absorption [ν_{max} (Nujol) 1718 cm.$^{-1}$] of the acid showing that the system (II) was not contained in a five- (or smaller) membered ring. The presence of a tertiary hydroxy-group (III) is suggested by (i) the infrared spectra of the acid [ν_{max} (Nujol) 3480 cm.$^{-1}$] and methyl ester [ν_{max} ($CHCl_3$) 3588 cm.$^{-1}$]; (ii) the n.m.r. spectrum of the methyl ester in $(CD_3)_2SO$ which showed no additional coupling compared to the spectra in $CDCl_3$ or CCl_4 solution; and (iii) the failure to prepare a trimethylsilyl ether of the methyl ester.[4]

The *gem*-dimethyl grouping (IV) is revealed by the presence of two sharp methyl signals (τ 9·01 and 8·84) in the n.m.r. spectrum of the acid and by high-resolution mass spectra of the acid and methyl ester which showed prominent peaks, with appropriate metastable ions, for the sequence *M/e* → *m/e* 83 [C_5H_7O (VIII)] → *m/e* 55 [C_4H_7 (IX)].

The remaining n.m.r. signals of the acid comprise an AB-quartet (6·42 and 6·11, J_{AB} = 7·5 c./sec.) and suggest the grouping (V) with an ether-oxygen since no other oxygen function is indicated by the spectroscopic data. Spin-decoupling experiments showed that one of the protons in the system (V) is coupled to one of the methylene protons in the grouping (II) with J = 3·5 and 2·0 c./sec., in the acid and methyl ester respectively.

The groupings (I)—(V) account for $C_{14}H_{20}O_5$ leaving one tetra-substituted carbon atom (VI). The low-field resonance of the δ-proton of the dienoic acid (I), similar to that found in abscisic acid (X),[5,6] suggests a vicinal oxygen function and leads to structures (XI) and (XII) as the most plausible of the many ways of combining groupings (I—VI). Detailed examination of the molecular composition of the fragment ions in the mass spectra of the acid and methyl ester favours the epoxide structure (XII), in particular the pathway shown in the Scheme where the structures are meant to be illustrative only.

In preliminary experiments, phaseic acid shows a weak but positive effect in the cotton abscission bio-assay, kindly determined by Professor F. T. Addicott. Unlike abscisic acid, it shows a plain negative o.r.d. curve $[\alpha]_D$ (MeOH) − 3350° (589 mμ) and −5950° (276 mμ), kindly determined by J. W. Cornforth, F.R.S. Methyl abscisate like methyl phaseate does not form a trimethylsilyl ether.



Two facts which are less readily accommodated in the tentative structure (XII) are (i) the magnitude of the long-range coupling constant between one of the epoxide protons and one of the α-methylene carbonyl protons and (ii) the failure as judged by the u.v. spectrum, to effect alkali-induced β-elimination of the epoxide oxygen to the $\alpha\beta$-unsaturated ketone. These points, and attempts to relate phaseic and abscisic acids chemically, are under investigation.

(*Received, December 4th,* 1967; *Com.* 1288.)

---

[1] J. MacMillan, J. C. Seaton, and P. J. Suter, *Tetrahedron*, 1960, **11**, 60.

[2] W. K. Rohwedder, A. R. Mabrouk, and E. Selke, *J. Phys. Chem.*, 1965, **69**, 1711.

[3] J. MacMillan and P. J. Suter, *Tetrahedron*, 1967, **23**, 2417.

[4] A. McCormick and S. L. Jensen, *Acta Chem. Scand.*, 1966, **20**, 1989.

[5] K. Ohkuma, F. T. Addicott, O. E. Smith, and N. E. Thiessen, *Tetrahedron Letters*, 1965, 2529.

[6] J. W. Cornforth, H. Draker, B. V. Milborrow, and G. Ryback, *Chem. Comm.*, 1967, 114.