Structure of Muristerone A, a New Phytoecdysone

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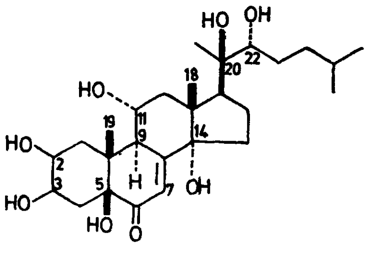
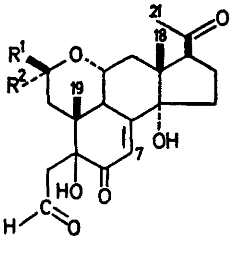
Summary Muristerone A, a new phytoecdysone isolated from *Ipomoea calonyction* (Choisy) Hallier f. sp. nova, has been identified as 2β,3β,5β,11α,14α,20*R*,22*R*-heptahydroxycholest-7-en-6-one.

The seeds of *Ipomoea calonyction* (Choisy) Hallier f. sp. nova† ("kaladana", formerly classified as *Ipomoea calonyction muricatum* G. Don[1]) contain, besides a large amount of ecdysterone, makistereone A, and ecdysone, a new phytoecdysone which is designated muristerone A (I).

Muristerone A,‡ m.p. 238—241° $[\alpha]^{20}_{D}$ + 49·6 (pyridine), forms a 2,3,11,22-tetra-acetate,‡ m.p. 236—238° and an amorphous 2,3; 20,22-diacetonide.‡ The u.v., i.r., and n.m.r. spectra indicate the presence in (I) of the usual 14α-hydroxy-7-en-6-one system,[2] and mass-spectrometric and n.m.r. evidence suggests that muristerone A possesses the same side-chain as ponasterone A.[3]



(I)



(II)a, R^1=H , R^2=OMe
b, R^1=OMe , R^2=H

One of the two hydroxy-groups present in the tetracyclic part of the muristerone A molecule in addition to the usual 2β-, 3β-, and 14α- hydroxy-groups, is located at the C-11 equatorial position, as suggested by the ease of acetylation and by the 9-H splitting pattern in the n.m.r. spectrum of the tetra-acetate (doublet of doublet at δ 3·54, *J* 2·5 and 9·0 Hz).

In agreement with this, the oxidation of (I) with periodic acid (2 equiv.) in MeOH gives a nearly equimolar mixture of the two epimeric compounds, (IIa) and (IIb).‡ This mixture appears to be homogeneous on t.l.c., but shows in its n.m.r. spectrum ($CDCl_3$) separate signals for the C-18, C-19, CH_3-O, MeO·C*H*O, and C-7 protons of the two compounds.

The remaining hydroxy-group is tertiary and its assignment to C-5 can be made on the basis of the chemical as well as the spectroscopic properties of (I) and its derivatives. The β-orientation of this hydroxy-group is established by the shift of the position of both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ Cotton-effect peaks in the c.d. curve of (I)[4] and by the shift of the unsaturated carbonyl stretching vibration from 1660 to 1680 cm^{-1} in all the muristerone A derivatives.[4,5]

Moreover, the c.d. curve of muristerone A 20,22-acetonide 2,3,11-tribenzoate,‡ m.p. 230—240°, obtained by selective acid removal of the 2,3-acetonide group from the diacetonide, followed by benzoylation, shows a very stong negative Cotton effect at 241 nm (Δε −38) and positive Cotton effect at 223 nm (Δε + 50), thus confirming the A/B *cis* ring-junction, the 11α-OH orientation, the β-orientation of the 2- and 3-OH, and the chair conformation of ring A.[6] The *cis*-relationship between the C-3 and the C-5 hydroxy-group was finally established by the formation of a 3,5-cyclic carbonate‡ (amorphous)[7] from muristerone A 20,22-acetonide 3,11-diacetate,‡ obtained by controlled acetylation of the 20,22-acetonide.

Preliminary experiments§ show that muristerone A possesses a very high moulting activity.

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‡ Spectral data are consistent with the suggested structure.

§ M. Martelli and P. Rota, Istituto di Entomolgia Agraria dell'Universita degli Studi di Milano, personal communication.

[1] M. L. Gupta, J. P. Tewari, S. N. Khanna, P. C. Gupta, M. C. Srivastata, and S. S. Mishra, *J. Pharm. Sci.*, 1967, **56**, 771.

[2] P. Karlson, H. Hoffmeister, H. Hummel, P. Hocks, and G. Spiteller, *Chem. Ber.*, 1965, **98**, 2394.

[3] M. Koreeda, D. A. Sohooley, K. Nakanishi, and H. Hagiwara, *J. Amer. Chem. Soc.*, 1971, **93**, 4084.

[4] M. Koreeda and K. Nakanishi, *Chem. Comm.*, 1970, 351.

[5] (a) H. Hikino, K. Nomoto, and T. Takemoto, *Tetrahedron*, 1970, **26**, 887; (b) J. Jizba, V. Herout, and F. Šorm, *Tetrahedron Letters*, 1967, 5139.

[6] M. Koreeda, N. Harada, and K. Nakanishi, *Chem. Comm.*, 1969, 548.

[7] G. Heinrich and H. Hoffmeister, *Tetrahedron Letters*, 1968, 6063.