

The Structure of Cimigenol

By STEFANO CORSANO

(Istituto di Chimica Organica dell'Università di Roma, Rome, Italy)

and JOHN M. MELLOR* and GUY OURISSON

(Institut de Chimie, Faculté des Sciences, Strasbourg, France)

WE now propose structure (I) for cimigenol, the triterpene genin of one of the xylosides extracted from *Cimicifuga racemosa* (*Actea racemosa*). The structure of ring A, and the position of the cyclopropane ring, have been deduced earlier,¹ as well as

the nature of the fragment (II) now assigned to C-24—C-27.

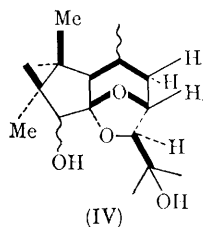
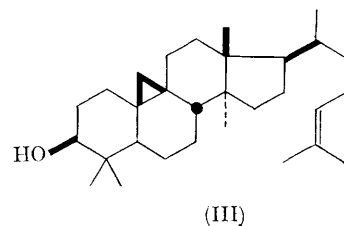
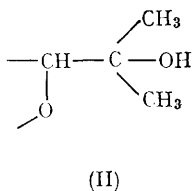
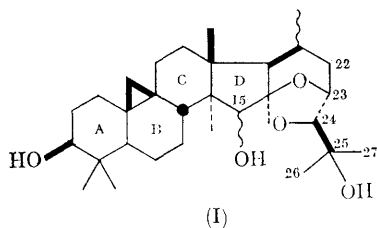
New results leading to formula (I) include the following:

The mass spectrum of cimigenol confirms the

* Present address: Chemistry Department, University of Southampton.

¹ S. Corsano and G. Spano, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1962, **32**, 674; S. Corsano, *Gazzetta.*, 1965, **95**, 117.

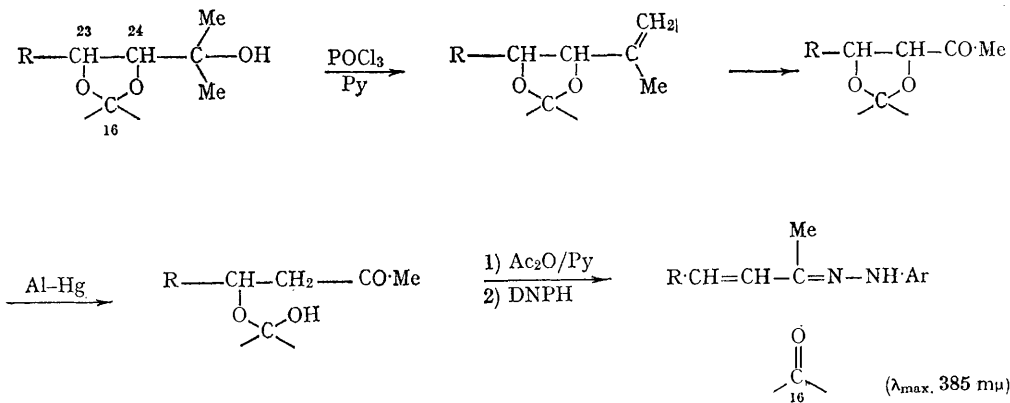
formula $C_{30}H_{48}O_5$ (m/e 488). The n.m.r. spectra of cimigenol and its derivatives are particularly revealing.² They show only *one* split signal [3H, $J = 5-6$ c./sec.] attributable to a secondary methyl group (confirmed by double irradiation)].



The proton at C-15 gives a singlet in the 15-acetates and a doublet in the 15-hydroxy-derivatives (a singlet after equilibration with D_2O); this signal disappears in the 15-ketones, which show the expected strong positive Cotton effect ($\Delta\epsilon = +1.8$). The i.r. spectrum of these 15-ketones [$\nu(C=O)$ 1765 cm^{-1}] is in agreement with the accumulation of C-O bonds α to the carbonyl.³

The oxygenation pattern in the side-chain and in ring D has been confirmed in the 3, 15-diacetate series by the following transformations partly described earlier¹:

The structural variations indicated, as well as others giving confirmatory evidence, have been obtained in several series (3-acetoxy, 3-deoxy, 3-ketone, 3, 15-diketone).



The signals of the protons at C-24 and C-23 show up clearly in the n.m.r. spectra of several derivatives (3,15-diacetates, 3-ketone, 3,15-diketone). That attributed to 23-H is a doublet ($J = 10$ c./sec.), very slightly split again ($J = 2$ c./sec.) with the same constant as that observed in the doublet

All the compounds obtained, in the various series mentioned, gave analytical values and n.m.r. spectra in agreement with the suggested structures. A direct correlation with cycloartenol (III) has however, not yet been achieved.

(Received, April 12th, 1965.)

² N.m.r. spectra have been determined in deuteriochloroform with a Varian A-60 spectrometer, using tetramethylsilane as internal standard.

³ *c.f. e.g.*, C. Sandris and G. Ourisson, *Bull. Soc. chim. France*, 1958, 338, 350.