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JATROPHOLONES A AND B, NEW DITERPENOIDS FROM THE ROOTS OF JATROPHA GOSSYPIIFOLIA (EUPHORBIACEAE) - CRYSTAL STRUCTURE ANALYSIS OF JATROPHOLONE B.

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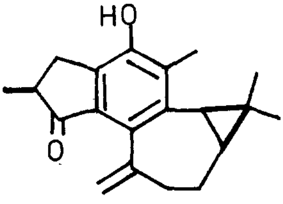
From the roots of Jatropha gossypiifolia (Euphorbiaceae) we have isolated two new diterpenoids, jatropholone A (1), $C_{20}H_{24}O_2$, and its C-2 epimer jatropholone B (2), with a cyclised casbene skeleton incorporating a fully substituted cresol ring. The structure of jatropholone B was established as (2) by a crystal-structure analysis of the corresponding acetate (3).



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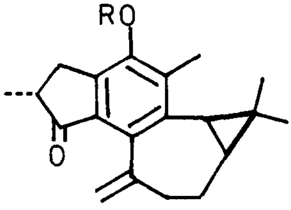
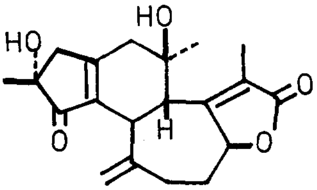


2 R=H
3 R=Ac



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The functionality of jatropholone B was revealed by its spectroscopic properties. The most notable feature was a fully substituted cresol ring [δ_C 150.2, 137.5, 137.2, 131.8, 131.1, 134.4, 28.2; δ_H 2.3 (3Hs), 5.42 (s, OH), λ_{max} 225, 238, 275, 335 nm in EtOH changing to 256, 296, 357 nm on addition of alkali; ν_{max} (CCl_4) 3603 cm^{-1}]. In addition there were two tertiary methyls and a secondary methyl [δ_C 17.1, 16.1, 13.3; δ_H 0.86, 1.29, 1.34, (d, J 7 Hz)], an exomethylene [δ_C 145.6, 115.2; δ_H 4.66, 5.19 (both bs)] and a ketonic carbonyl [δ_C 208.2; ν_{max} (CCl_4) 1715 cm^{-1}]. These accounted for six of the nine double bond equivalents and hence the molecule was tricarbocyclic in addition to the aromatic ring. A singlet at δ 19.5 and two doublets at δ 29.4 and 21.5 in the off-resonance spectrum of (2) indicated a cyclopropane ring and suggested that the jatropholones were based on a cyclised casbene skeleton.[1] Since there was insufficient material to allow a detailed chemical investigation jatropholone B acetate was subjected to X-ray crystallographic analysis which revealed the structure as (3).

For the X-ray analysis a small crystal of Jatropholone B was exposed to graphite-monochromated Mo radiation on a Hilger & Watts Y290 diffractometer, and the intensities of 1766 independent reflexions [$\underline{I} \geqslant 2.5\sigma_{\underline{I}}$] were measured using the θ,ω-scan technique in the range 2θ $0-58^{\circ}$. The intensities were corrected for Lorentz and polarisation factors, but absorption effects were ignored. The structure was resolved by direct methods using the suite of programs MULTAN (1974), and has been refined by full-matrix least-squares calculations to a final $\underline{R}$ of 0.035. Positions were determined for the hydrogen atoms from difference syntheses, and were refined in the latter stages of the least-squares calculations.

The spectroscopic properties of jatropholone A (1) indicated a close similarity to jatropholone B. Separation of the two isomers required careful chromatography. Their epimeric relationship at C-2 followed from the fact that mild base treatment of either compound afforded an equimolar mixture of both.

The absolute configuration of the jatropholones was not established. The cd curves of both compounds were virtually identical but difficult to interpret in the absence of suitable model systems. It is reasonable to assume that (1) and (2) have the absolute configuration which is common to similar diterpenoids e.g. bertyadionol[2] and epoxylathyrol[3] from the Euphorbiaceae.[4] The jatropholones represent a new skeletal type of diterpenoid closely akin to crotofolin A (4).[5] Previous work on Jatropha species resulted in the isolation of jatrophone[6] and jatrophatrione[7] both of which exhibited significant antitumour activity. The jatropholones were inactive.

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