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X RAY STRUCTURE OF BETHANCOROL, A NEW COUMARIN FROM CNEORUM TRICOCCUM

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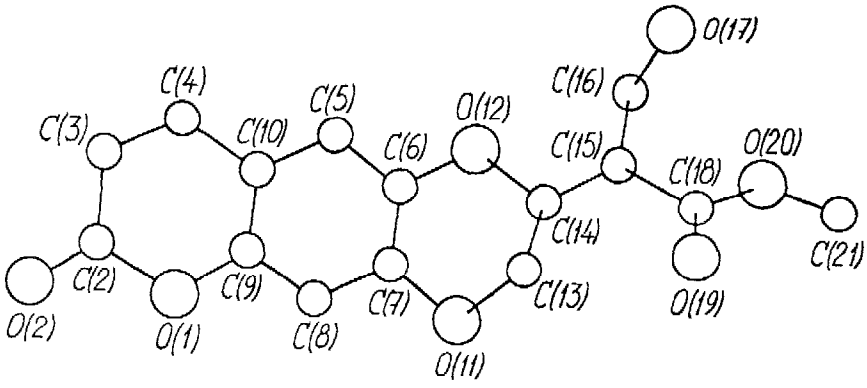
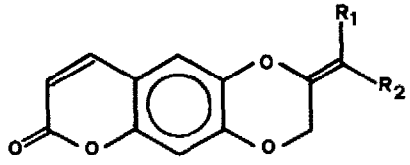
Further to our papers [1,2], we are now reporting bethancorol, a new coumarin (1a) mp 190-192°, $C_{15}H_{12}O_7$ (M^+ 304), λ_{max}^{EtOH} 230, 262, 336 nm. Its UV and IR spectra show a coumarin nucleus. In the NMR ($CDCl_3$), two doublets at 6.38 and 7.58 δ (J 10Hz each) indicate a coumarin ring, singlets at 6.94 and 7.12 δ, aromatic protons in C-5 and C-8, another singlet at 3.80 (3H), a methoxyl group and those at 5.26 and 4.58 (2H each), $-O-CH_2$ and $-CH_2-OH$ groups. The signal at 4.58 shifted to 5.28 on adding a drop of TAI.[3] These data are compatible with structure 1a, 2a, 1b or 2b for bethancorol, determined as 1a by x ray analysis.

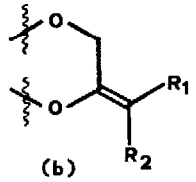
Bethancorol crystallizes in a triclinic cell with a = 8.201 (1), b = 12.186(2), c = 7.118 (1) Å, α = 96.84 (3), β = 107.53 (2), γ = 96.61 (3)°, z = 2. A fully automatic diffractometer with monochromated MoK_α radiation was used to collect the intensities of 3839 independent reflexions for $\theta \leq 30°$. 2092 were observed $I > 2\sigma(I)$ and used for the structure refinement. Calculated values for $\langle|E^2-1|\rangle$ and $\langle|E|\rangle$, 1.074 and 0.748, show a hypercentric diffraction compared with the theoretical values for a centric distribution: 0.968 and 0.798 respectively. This hypersymmetry stems from the high pseudosymmetry in both planar molecules related by a crystallographic centre. The space group $P\bar{1}$ was confirmed by the least squares refinement. This hypercentric structure's special diffraction pattern made it difficult to solve by direct methods. Using the Multan 74 System [4], a good molecular fragment was found, but shifted from its real position. A Pl difference map sited the fragment in relation to the crystallographic inversion centre. The whole molecule was anisotropically refined to



an R of 0.096 [4], standard deviations in bond distances and angles being 0.007 Å and 0.4°. The figure shows the molecular structure, double bonds being C(2)O(2) = 1.20, C(3)C(4) = 1.33, C(14)C(15) = 1.34 and C(18)O(19) = 1.19 Å. The molecule may be described as a natural isoprene C(13)C(14)C(15)C(16)C(18) attached to the coumarin nucleus through O(11) and O(12). Both fragments are almost planar with a dihedral angle of 24°. All bond distances and angles appear normal. The molecules are linked by weak hydrogen bonds O(17)H(17)...O(2) of 2.95 Å.



(a)



(b)

	R_1	R_2
1	CH_2OH	COOMe
2	COOMe	CH_2OH

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