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NEW COMPOUNDS FROM BALLOTA HISPANICA. X-RAY CRYSTAL AND MOLECULAR STRUCTURE OF HISPANONIC ACID METHYL ESTER (MEAH)

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Summary. The structure and absolute configuration of a novel diterpenoid (MEAH) has been determined.

MEAH ($C_{21}H_{26}O_4$) is a natural product isolated from Ballota hispanica[1] and characterized as a novel diterpenoid. It presents a new hydrocarbon skeleton. The determination of its structure and absolute configuration is interesting for this reason.

The X-ray spectrum shows orthorhombic symmetry, space group $P2_12_12_1$, a=22.036(2), b=10.529(1), c=7.809(3) Å, V=1811.8(2) Å^3, Z=4, D_c=1.25 g cm^{-3}, $\mu(CuK_\alpha)$=6.968 mm^{-1}.

The structure was solved by MULTAN[2] and refined anisotropically by least squares. An appropiate weighting scheme was chosen to give flat dependence of $<w(Fo-Fc)^2>$ v.s. $<\sin\theta/\lambda>$ and v.s. $<Fo>$[3]. Final refinement gave R=.044 and $R_w=(\Sigma w\Delta^2/\Sigma w|Fo|^2)^{1/2}=.041$.

The anomalous dispersion effect of the oxygen atoms was used to establish the absolute configuration of the molecule shown in figure 1. A careful remeasurement of the 21 more relevant Bijvoet pairs with Fo>10.σ(Fo) $|\Delta|Fc||>0.08$ and $|\Delta|Fo||>0.03$ gives the following discrepancy indices[4]:
average Bijvoet difference $R_1=\Sigma||Fo(+h)-Fo(-h)|-|Fc(+h)-Fc(-h)||/N=0.032$ (0.229 for the reversal enantiomorph), average Bijvoet ratio $R_2=\Sigma|Ro-Rc|/N=0.007$ (0.040) and $R_3=\Sigma|\Delta Io-\Delta Ic|/\Sigma|\Delta Io|=0.241$ (2.034), with N = number of Bijvoet pairs, $Ro=\Delta Io/<F^2o>$, $Rc=\Delta Ic/<F^2c>$, $\Delta Io=F^2o(+h)-F^2o(-h)$ and $\Delta Ic=F^2c(+h)-F^2c(-h)$.

The A ring has a chair conformation. The chiral center C(4) has a S absolute configuration. Carbomethoxyl and angular methyl groups are in axial positions. Steric interaction between these groups could be responsible of the long bond distances C(1)-C(10)=1.552(3), C(10)-C(5)=1.548(3) and C(4)-C(5)=1.570(3) Å.

The B ring has a half-chair conformation. The junction between the B and C rings is an unsaturated one.

The C ring has a twisted boat conformation with C(8), C(9), C(12), C(13) nearly in the same plane (deviations of these atoms from the least-square plane are .03 Å for C(8) and C(12) and -.03 Å for C(9) and C(13)). Atoms C(11), C(16) and C(17) are at the same side of this plane. The carbonyl group C(17)-O(2) is between the two double bonds C(8)-C(9) and

C(13)-C(16), but only the double bond in the furan ring is conjugated with the carbonyl group. (C(13), C(16), C(17) and O(2) are in the same plane).

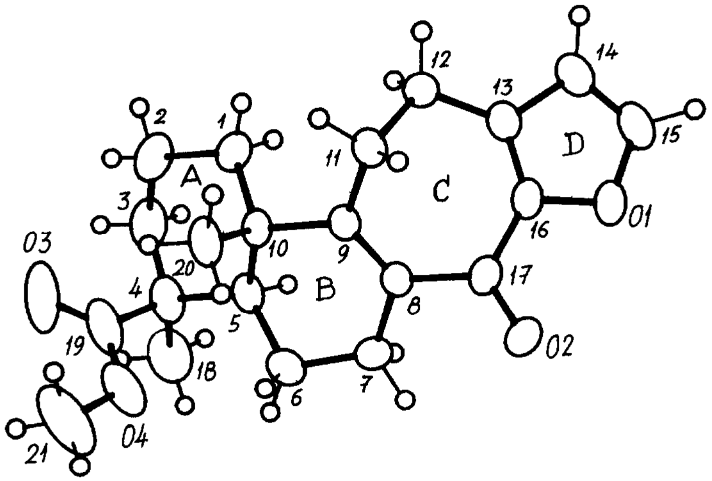
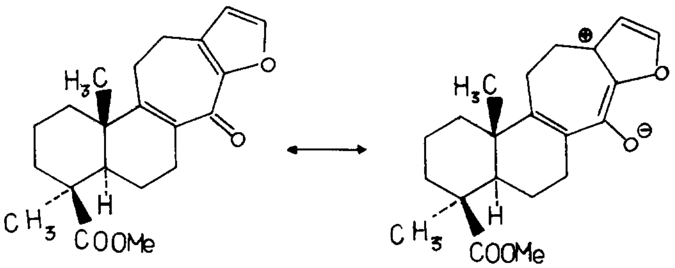


Figure 1. X-ray model of MEAH, showing its absolute configuration.

The bond distances C(13)-C(16)=1.361(3) v.s. C(14)-C(15)=1.329(3) in the furan ring and C(17)-O(2)=1.222(3) v.s. the normal value 1.18, are remarkable. Moreover double bond character in C(16)-C(17)=1.459(3) v.s. C(8)-C(17)=1.504(3) indicates that the compound could be represented by some polar canonical formule which implicates a low density charge on C(13). The furan ring is planar.



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