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RUPESTRALIC ACID , A NEW DITERPENE LACTONE

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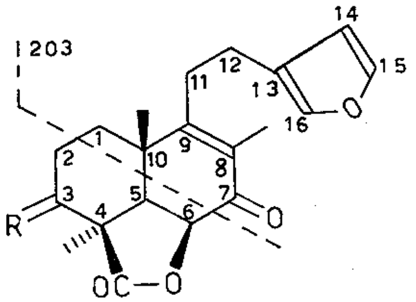
Rupestralic acid, extracted from Ballota rupestris (Labiatae) is assigned structure [III]-[IV]. The reaction with diazomethane yields an unstable epoxy ester [V] which changes either into the methyl ketone [VI] or into the lactone [VII]. An interesting fragmentation is evidenced in the mass spectra of such compounds.

During our present investigations on the diterpenes from medicinal plants of Southern Italy, we isolated from Ballota rupestris Vis. (Labiatae) the furanic diterpenes ballonigrin [I][1] and ballonigrinone [II][1]. We report here on the structure of a minor extractive from this species. The occurrence of this product in exceedingly poor quantity required the use of spectroscopic elucidation almost exclusively.

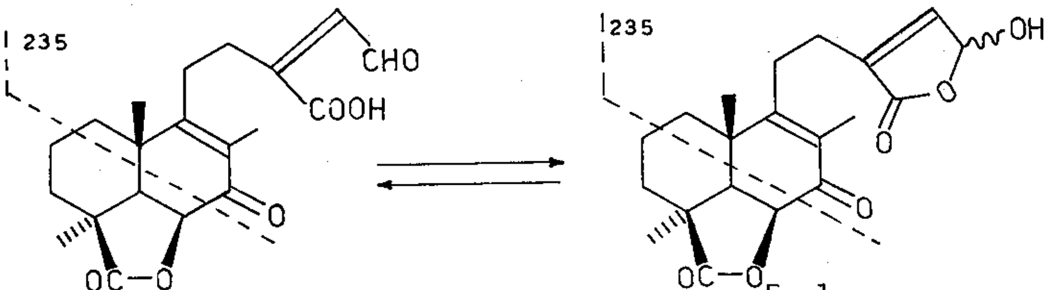
The product, named rupestralic acid, has molecular formula $C_{20}H_{24}O_6$, m.p. 186° (from ethyl acetate), and is soluble in alkali. It can be represented by [III] or better by the tautomeric structure [IV]. Its mass spectrum showed peaks at m/e 360 (M^+), 342, 235 (100%), 233, 109, 91.

Owing to the poor solubility of the acid in $CDCl_3$ and acetone-d_6, all the product available (30 mg) was treated with ethereal solution of diazomethane at the aim of preparing a more soluble



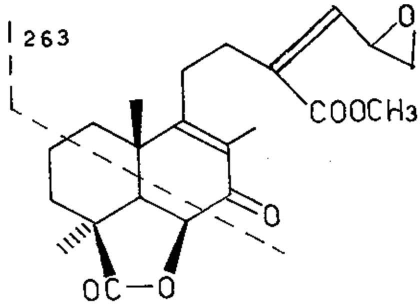
[I] $R = H_2$

[II] $R = O$

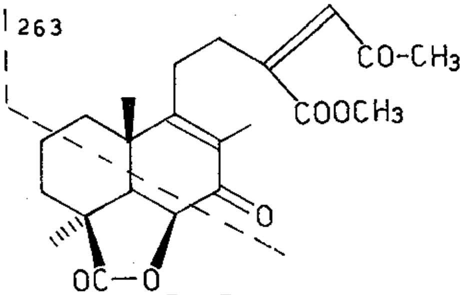


[III]

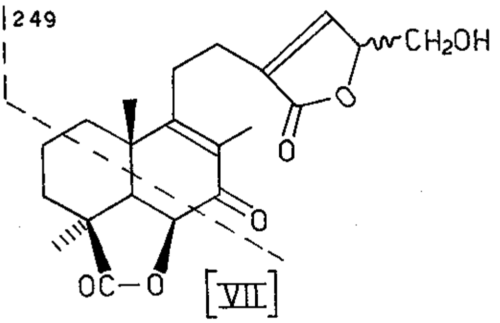
[IV]



[V]



[VI]



[VII]

methyl ester and registering its NMR spectrum. The mass spectrum of the oily product indicated a $C_{22}H_{28}O_6$ formula, arising from the reaction with two moles of diazomethane; peaks occurred at m/e 388 (M^+), 356, 263, 233, 231, 141, 111 (100%), 109. The UV spectrum (ethanol) showed two strong absorptions λ_{max} 258 nm (ε 9000) and 226 nm (ε 9300), whereas the IR spectrum had bands at 1770, 1710, 1680 cm^{-1}.

The NMR spectrum (60 MHz, $CDCl_3$)had signals at δ 1.06 and 1.33 (s, t.CH_3), 1.85 (s, olefinic CH_3), 2.17 (d, J 6.2 Hz, H-5), 2.40 (apparent s, CH_2CH_2), 2.65 (q, J 5.3 and 2.6 Hz, H_{epoxy}), 3.08 (q, J 5.3 and 4.5 Hz, H_{epoxy}), 3.80 (s, $COOCH_3$), 4.20 (ddd, J 8.3-2.6-4.5 Hz, H-15), 4.67 (d, J 6.2 Hz, H-6), 5.55 (d, J 8.3 Hz, H-14). All these data were consistent with the structure [V].

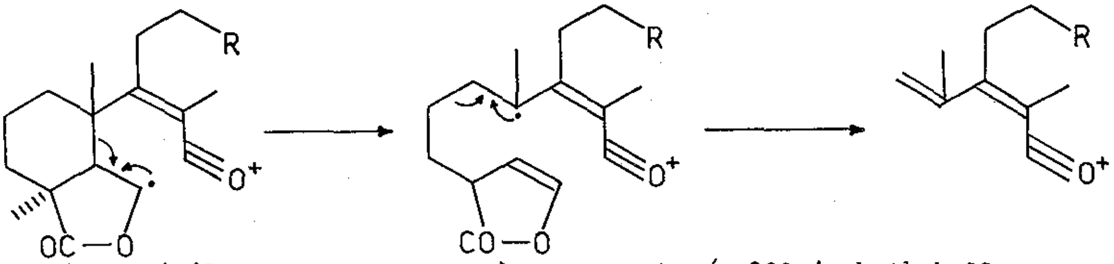
The product underwent a slow, spontaneous transformation leading to an isomeric compound and to a $C_{21}H_{26}O_6$ product: they were separated by chromatography easily and assigned the structures [VI] and [VII] respectively.

The mass spectrum of [VI](oily) had the main peaks at m/e 388 (M^+), 356, 329, 263 (100%), 231, 109. Its NMR spectrum (100 MHz, $CDCl_3$) showed signals at δ 1.06 and 1.31 (s, t.CH_3), 1.96 (s, olefinic CH_3), 2.33 (s, $COCH_3$), 2.23 (d, J 6 Hz, H-5), 3.85 (s, $COOCH_3$), 4.72 (d, J 6 Hz, H-6), 7.17 (broad s, H-14).

The peaks in the mass spectrum of [VII](oily) occurred at m/e 374 (M^+), 356, 249 (100%), 233, 109, 91. In its NMR spectrum (100 MHz, $CDCl_3$) the singlet of carbomethoxy group at 3.8 δ was missing: signals occurred at δ 1.08 and 1.32 (s, t.CH_3), 1.87 (s, olefinic CH_3), 2.25 (d, J 6 Hz, H-5), 3.8-4.2 (m, $\underline{CH_2}OH$), 4.75 (d, J 6 Hz, H-6), 5.10 (m, H-15), 7.17 (m, H-14).

The above evidence established the structures of rupestralic acid and its derivatives.

The base peaks occurring at m/e 235 in [III], at 263 in [VI], at 249 in [VII], and the strong peak at 263 in [V], are worthy of remark. They can be attributed to the fragmentation reported in the schema:



As a similar very strong peak occurs at m/e 203 in both ballonigrin [I] and ballonigrinone [II], this pattern seems to be typical of these 7-keto-labd-8-ene structures.

The co-occurrence of rupestralic acid and ballonigrin in Ballota rupestris prompts the question of their biogenetical connection; indeed, [III] could be either a precursor or a degradation product of ballonigrin.

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References and notes

1. G.Savona, F.Piozzi, J.R.Hanson, and M.Siverns, J.C.S.Perkin Trans. I, 1977, 322.
2. Compare the values 7.10-7.17 δ found for neoandrographolide and derivatives, by W.R.Chan, D.R.Taylor, C.R.Willis, and H. W.Fehlhaber, Tetrahedron Letters, 1968, 4803.

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