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THE STRUCTURE OF SOLIDAGONIC ACID,
A BITTER PRINCIPLE OF GOLDENROD

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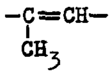
A bitter principle, solidagonic acid, $C_{22}H_{34}O_4$, was isolated from root of goldenrod, Solidago altissima L.. Solidagonic acid (I), mp 143-144°C, $(\alpha)_D^{12}$ -97.6°*, is a monobasic carboxylic acid ($\nu_{C=O}$1680cm^{-1}, $\nu_{C=C}$1637cm^{-1}, ν_{O-H}3400-2400cm^{-1}, δ 11.75 (1H), its methyl ester (II), $C_{23}H_{36}O_4$, mp 106.5°C, $(\alpha)_D^{12}$-98.8°), having an acetylated secondary hydroxyl group (NMR** of II : δ 2.00 (3H singlet), δ near 5.05 (1H)). The presence of two tertiary methyl groups (3H singlet at δ 0.97 and 1.18), a secondary methyl group (3H doublet centered at δ 0.91, J=7c/s) and  $-\underset{\mathrm{CH_3}}{\overset{}{\mathrm{C}}}{=}\mathrm{CH}-$ group (3H singlet at δ 1.73, 1H broad signal at δ near 5.05) was detected clearly from the NMR spectrum of II. The conjugation of the carboxyl group and the ethylenic linkage was borne out from the UV spectrum of II : λ_{max} 217.5mμ (ε 15400). A broad singlet (1H) centered at δ 5.56 and a doublet (3H, J= 1.2c/s) at δ 2.15 can be reasonably assigned to an α-vinyl hydrogen and a β-vinyl methyl group to the carbomethoxyl group, respectively. This was further confirmed by the NMR spectrum of the derived alcohol ($LiAlH_4$ reduction) when these signals, as expected, shifted upfield (to δ 5.31 and δ 1.65). Oxidation of II with 1 mole monoperphthalic acid gave a monoepoxide (III), mp 135.5-136.5°C, and its reduction with $LiAlH_4$ afforded a triol (IV), mp 120-121.5°C. The diacetate of IV gave a methyl ketone (V), mp 104-105°C, (δ 2.10, $\nu_{C=O}$1705cm^{-1}) by ozonolysis. It is clear

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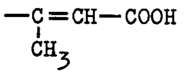
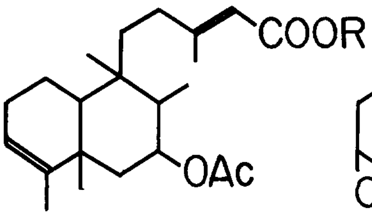
* All rotations have been measured in 95% ethanol solution.

** The NMR spectra were taken on about 10% solutions in CCl_4 or $CDCl_3$ on a JEOL C-60 spectrometer; the signals are recorded in ppm from tetramethylsilane (internal standard) as zero.

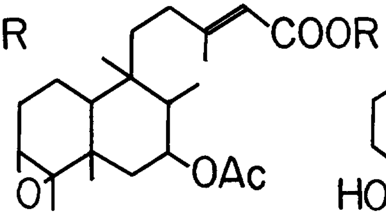
from these results that solidagonic acid has  $-\underset{CH_3}{C}=CH-COOH$ group.

1,2,5-Trimethylnaphthalene was formed on dehydrogenation of the ester II with 10% Pd-C or Se. The monoepoxide III on treatment with CH_3MgBr gave the triol (VI) and on dehydrogenation of the latter with 10% Pd-C resulted the formation of 1,2,5,6-tetramethylnaphthalene.

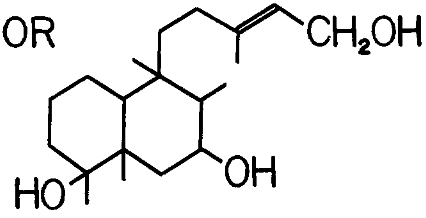
A tetrahydroderivative, which has been prepared by hydrogenation of the ester II, gave the hydroxy acid (VII) on saponification. Oxidation of VII with Jones reagent gave a keto acid (VIII), mp 82-83° C. Treatment of VIII with CH_3MgBr followed by dehydrogenation with Se gave 1,2,3,5-tetramethylnaphthalene. A possible structure for solidagonic acid accommodating all of the above results is illustrated in (I), and this rearranged bicyclic diterpenoid skeleton is supported by biogenetic considerations (1,2).



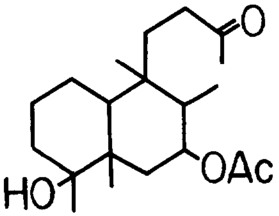
I R=H, II R=CH_3



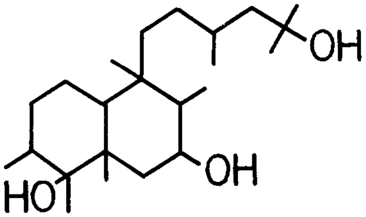
III R=CH_3



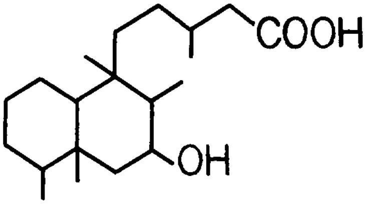
IV



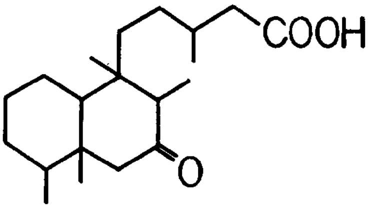
V



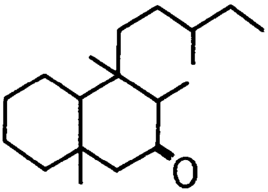
VI



VII



VIII



IX

The structure of I was confirmed by the NMR spectrum of the derived saturated ketone (IX) ($LiAlH_4$ reduction of II, catalytic hydrogenation and then oxidation with Jones reagent). The NMR spectrum of IX showed the presence of three hydrogens in α positions of the ketonic group. A quartet (1H, J=6.7c/s) centered at δ 2.47 is assigned to a hydrogen at C-8 which is coupling only three hydrogens in a methyl group, and the AB-type two doublets centered at δ 1.95 and δ 2.28 (J=12c/s) are assigned to two hydrogens at C-6, which does not couple with the other hydrogen.

The stereochemistry of solidagonic acid has not been defined but its NMR spectrum would suggest that the allylic methyl group (δ 2.18) of the side chain must be cis to the carboxyl group (3,4).

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