

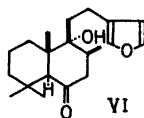
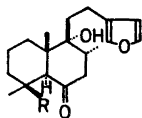
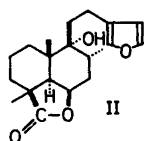
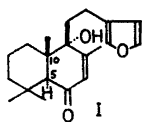
The Constitution and Stereochemistry of Solidagenone

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We have proposed¹ a structure (I; without stereochemistry) for solidagenone, a diterpenoid from the roots of *Solidago canadensis* L. We now present evidence which confirms this structure and in addition leads to an assignment of its stereochemistry (as in I).

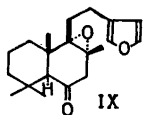
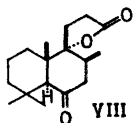
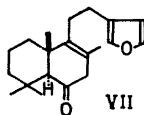
Our initial approaches to this end envisaged correlation of solidagenone with marrubiin² (II), by converting both into the dihydrosolidagenone (III). This compound, m.p. 89–90°, was prepared from marrubiin *via* the keto-aldehyde² (IV), by reduction of the derived oily thioacetal (V)



III R=CH₃

IV R=CHO

V R=CH(SCH₂)₂



with Raney nickel in acetone. We have not yet found conditions whereby solidagenone can be reduced to compound (III). The dihydro derivative, solidaganone (VI), m.p. 110–111°, isolated from lithium aluminium hydride or catalytic (H₂; Pd/C; ethanol; triethylamine) reduction has a C₈ axial methyl group (NMR evidence to be detailed in a full paper). These conditions also gave products of further reduction. However, the major product from lithium-ammonia and zinc-acetic acid reduction of solidagenone was the $\beta\gamma$ -unsaturated ketone (VII), m.p. 78–79°, [α]_D +139°, identical (mixed m.p., IR, UV, NMR, TLC, and mass spectrum) with the more abundant enone, m.p. 77–79°, [α]_D +132°, from phosphoryl chloride-pyridine dehydration of the ketol (III) from marrubiin. This, along with the observation that oxidation of solidaganone (VI) with chromic acid-acetic acid gave a keto- γ -lactone (VIII), m.p. 148–149°, ν_{\max} (CCl₄), 1782 and 1716 cm⁻¹, confirms the structure of solidagenone and proves the absolute configurations at C₈ and C₁₀.

The configuration at the remaining asymmetric centre (C₉) was derived as follows. The enone (VII) with *m*-chloroperbenzoic acid in chloroform gave one furan-containing epoxide (IX), m.p. 54–55°, which was smoothly isomerised in 85% yield to solidagenone (I) with β -naphthalenesulphonic acid in refluxing benzene. Formation of the α -epoxide and thus ring opening to a 9 α -hydroxyl group can be predicted on the basis of earlier work³ with closely analogous compounds.

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2. Appleton, R. A., Fulke, T. W. B., Henderson, M. S. and McCrindle, R. *J. Chem. Soc. (C)* **1967**. *In press*.
3. For leading references see Mangoni, L. and Adinolfi, M. *Gazz. Chim. Ital.* **97** (1967) 66.

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