The Structure of Solidagenone

By T. ANTHONSEN, P. H. MCCABE, R. MCCRINDLE, and R. D. H. MURRAY

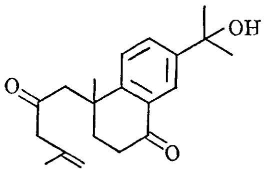
(*Organic Chemistry Laboratories, Norway Institute of Technology, Trondheim; and Chemistry Department, University of Glasgow, Glasgow, W.2*)

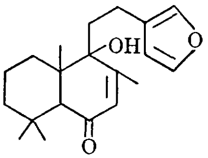
RECENTLY one of us has refuted[1] the suggestion[2] that the diterpenoid $C_{20}H_{28}O_3$, m.p. 131—132°, isolated[2,3] from certain *Solidago* species, has the structure (I). We now suggest structure (II) for this compound (solidagenone) on the basis of its molecular formula and the following spectroscopic and chemical evidence.

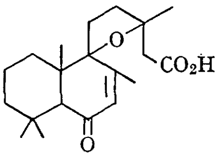
The presence of a β-substituted furan has been deduced[1] from the i.r. and n.m.r. spectra, while in the mass spectrum a strong $M-124$ peak may indicate[1] scission of a normal terpenoid ring A, which has no oxygen substituents.

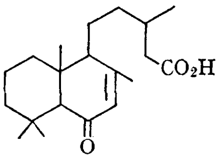
The $\alpha\beta$-unsaturated ketone is apparent from the carbonyl absorption at 1678 cm.$^{-1}$ (in CCl_4) in the i.r., although in the u.v. the enone absorption is masked in a broad composite band, λ_{max} (EtOH) 223μ mμ (ϵ 10,000). However, a narrow band, λ_{max} (EtOH) 234 mμ (ϵ 9800), results when the furan absorption of a similar compound, marrubiin,[4] λ_{max} (EtOH) 212 mμ (ϵ 5300), is subtracted. The derived maximum is consistent with structure (II) since the γ-hydroxyl group should have a hypsochromic effect.[5,6] The methyl group on the double bond appears as a doublet at τ 7·98 in the n.m.r. spectrum. Its coupling ($J\sim1$ c./sec.) to the α-vinyl proton has been confirmed by double-irradiation experiments.

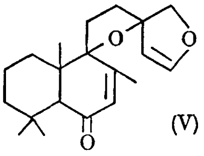
The presence of a hydroxyl group in solidagenone, in close proximity to the furan ring, is suggested by the i.r. absorption (in CCl_4) at 3611 (free) and 3567 (OH–π) cm.$^{-1}$ and confirmed by n.m.r. data, a concentration-dependent peak (–OH; one proton


(I)


(II)


(III)


(IV)


(V)

singlet) at about τ 8 disappearing when the sample is shaken with D_2O. Furthermore, this hydroxyl group is tertiary since there is no resonance in the n.m.r. attributable to a proton of the type *H*–C–OH. The n.m.r. also discloses three quaternary methyls (3H singlets at τ 8·99, 8·85, and 8·81) and a singlet at τ 7·28 (1H) is attributed to the hydrogen at C-5.

Structure (II) for solidagenone also readily accommodates the chemical data.[1] Thus the failure to form derivatives of the tertiary hydroxyl and the sterically hindered ketone [*cf.*, 6-oxogrindelic acid (III)[5] and 6-oxocativic acid (IV)[7]] is expected, as is the formation[7] of a saturated ketone on lithium aluminium hydride reduction. Finally, structure (II) is biogenetically plausible since 6-oxogrindelic acid is present[5] in a member of the *Grindelia* genus (*robusta*) which is closely related to *Solidago.*

Solidagenone may well be an artefact. In our hands, concentration of a light-petroleum extract of a *Solidago* hybrid resulted in the deposition of of crystalline material, m.p. 108—110°, which contained no solidagenone, and which is, on spectral evidence, a mixture (approximately 1 : 1) of two compounds (V; epimers at C-13). Further concentration of the mother liquors gave small amounts of solidagenone, which significantly could also be obtained in high yield by refluxing an ethanolic solution of the mixed ethers (V). These findings may explain the apparent change[2,3] in m.p. of solidagenone on recrystallisation. Work is in progress on the stereochemistry of solidagenone and on the structure and stereochemistry of several other diterpenes present in the root extracts of *Solidago* species.

(*Received, September 9th,* 1966; *Com.* 674.)

---

[1] T. Anthonsen, *Acta Chem. Scand.*, 1966, **20**, 904.
[2] H. Gerlach, *Pharmazie*, 1965, **20**, 523.
[3] F. G. Houston and R. C. Burrell, *Arch. Biochem.*, 1948, **16**, 299.
[4] J. W. B. Fulke and R. McCrindle, *Chem. and Ind.*, 1965, 647.
[5] L. Mangoni and M. Bellardini, *Gazzetta*, 1962, **92**, 983.
[6] T. G. Halsall, W. J. Rodewald, and D. Willis, *J. Chem. Soc.*, 1959, 2798.
[7] T. G. Halsall and M. Moyle, *J. Chem. Soc.*, 1960, 1324.