

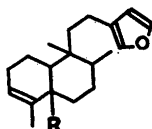
Furan-Containing Diterpenoids from *Solidago serotina* Ait.

T. ANTHONSEN, M. S. HENDERSON,
A. MARTIN, R. McCRINDLE and
R. D. H. MURRAY

Organic Chemistry Laboratories, Norway
Institute of Technology, Trondheim, Norway,
and Chemistry Department, The University of
Glasgow, Glasgow, W.2. Scotland.

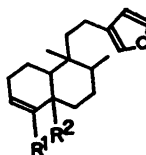
We have isolated from the roots of *Solidago serotina* Ait. several new diterpenoids and now report some preliminary studies on those which contain a furan moiety (see Table 1). We present evidence which allows a tentative assignment of structure to the compounds I–VI.

In solidagoic acid A (I) the following structural features are readily recognisable in its NMR spectrum: a β -substituted furan (τ 2.75, 2.94, 3.82; 1H each; broadened *s*),

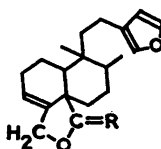


- I R = CO₂H
III R = CHO
IX R = CO₂Me
X R = CH₂OH
XVI R = CH₂OAc

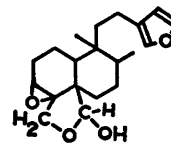
a proton and a methyl group attached to an olefinic bond (τ 4.45; 1H; unresolved *m*; W_{1/2} = 11 cps; 8.48; 3H; broadened *s*), one



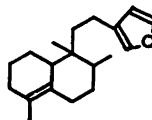
- II R¹ = CH₂O angeloyl; R² = CO₂H
IV R¹ = R² = CH₂OH
VI R¹ = R² = CHO
VII R¹ = CH₂OH; R² = CH₃
XIV R¹ = CH₂O angeloyl; R² = CO₂Me
XV R¹ = R² = CH₂OAc



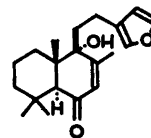
- V R = H, OH
XIII R = O



VIII



XI



XII

Table 1. Furan-containing diterpenoids from *Solidago serotina* Ait.

Compound No.	Molecular formula ^a	m.p.	$[\alpha]_D^{20}$ (EtOH)	$\nu_{\text{max}}^{\text{CCl}_4}$ (cm ⁻¹)
I	C ₂₀ H ₂₈ O ₃	169–171°	–58°	3500, 1692, 875
II	C ₂₅ H ₃₆ O ₅	134–135°	–28°	3500, 1720, 1695, 875
III	C ₂₀ H ₂₈ O ₂	oil ^b	–161°	2690, 1722, 875
IV	C ₂₀ H ₃₀ O ₃	oil ^b	–51°	3620, 3340, 875
V	C ₂₀ H ₂₈ O ₃	ca. 20° ^b	–30°	3600, 3380, 872
VI	C ₂₀ H ₂₆ O ₃	103–105°	–46°	2690, 1722, 875
VII	C ₂₀ H ₃₀ O ₂	oil ^b	–45°	3620, 3400, 875
VIII	C ₂₀ H ₂₈ O ₄	oil ^b	–47°	3600, 3400, 872

^a All compounds give satisfactory analytical values.

Dr. C. R. Enzell, Stockholm, kindly determined the mass spectra of I and II.

^b Oils were purified by TLC and then distilled at 120°C/0.005 mm.

tertiary (τ 9.02; 3H; *s*) and one secondary C-methyl group (τ 9.11; 3H; *d*; $J = 6$ cps). The oily methyl ester (IX) of A, $C_{21}H_{30}O_3$, $[\alpha]_D - 67.5^\circ$, $\nu_{\max} 1728 \text{ cm}^{-1}$, was readily converted by reduction with lithium aluminium hydride into the corresponding alcohol (X), $C_{20}H_{30}O_2$, $[\alpha]_D - 37.5^\circ$, $\nu_{\max} 3630 \text{ cm}^{-1}$, which also failed to crystallise. In this latter compound and the derived aldehyde (III), which also occurs naturally, the $-CH_2OH$ (τ 6.37, *d*; 6.51, *d*; 1H each; $J = 11$ cps) and $-CHO$ (τ 0.54; *s*) resonances respectively show no vicinal spin-spin coupling. Further, the presence of a $\beta\gamma$ -unsaturated acid grouping in A was shown by its smooth conversion at $280^\circ\text{C}/0.1 \text{ mm}$ into the nor-olefin (XI), $C_{19}H_{28}O$, $[\alpha]_D - 32.5^\circ$, which showed three $C-CH_3$ resonances at τ 9.13 (3H; *s*; *tert.*), 8.95 (3H; *d*; $J = 7$ cps; *sec.*), and 8.35 (3H; broadened *s*; vinyl) and, significantly, no vinyl proton signals.

This evidence bearing in mind that the labdane-related diterpenoid, solidagenone¹ (XII) occurs in *S. canadensis* L., would appear to indicate a rearranged labdane skeleton² for solidagoic acid A and thus the constitution (I).

The marked similarity of the NMR spectra of solidagoic acids B (II) and A (I) suggests that the former differs solely in that the vinyl methyl has been replaced by an allylic primary alcohol present as its angelate ester. Thus there are resonances in the NMR spectrum of acid B, $\lambda_{\max}^{\text{EtOH}}$ 221 $m\mu$ ($\log \epsilon$ 3.78), at τ 5.50 (2H; *s*; $-CH_2O-$) and 3.96, 7.95–8.15 (1H and 6H, respectively; typical³ angelate pattern). Moreover, pyrolysis of acid B at $320^\circ\text{C}/0.01 \text{ mm}$ afforded angelic acid, m.p. 45°C (also identified by GLC; 10% FFAP, 125°C) and the oily γ -lactone (XIII), $C_{20}H_{28}O_3$, $\lambda_{\max} 1778 \text{ cm}^{-1}$.

The formation of this lactone provides further support for the proposed structure of acid A which has been correlated with B as follows. Reduction of the oily methyl ester (XIV) of B, $C_{26}H_{38}O_6$, $[\alpha]_D - 25^\circ$, $\nu_{\max} 1728 \text{ cm}^{-1}$, with lithium aluminium hydride led to the diol (IV) which also occurs naturally. The derived diacetate (XV), $C_{24}H_{34}O_8$, $[\alpha]_D - 44^\circ$, on hydrogenolysis ($H_2/Pd/EtOH/NEt_3$) gave the monoacetate (XVI), $C_{23}H_{32}O_7$, $[\alpha]_D - 50^\circ$, which has also been obtained by direct acetylation of alcohol (X).

Tentative structures for the hemiacetal (V) and dialdehyde (VI) follow from their conversion with lithium aluminium hy-

dride into the diol (IV), while the chemical and spectroscopic evidence is compatible with structures (VII) and (VIII) for the remaining two diterpenoids of natural provenance.

Acknowledgement. Maintenance grants from *Norges Almenvitenskapelige Forskningsråd* (T.A.) and the *Science Research Council* (M. S. H. and A.M.) are gratefully acknowledged. We thank Dr. A. M. M. Berrie, Department of Botany, Glasgow, for identifying *S. serotina* Ait.

1. Anthonson, T., McCabe, P. H., McCrindle, R. and Murray, R. D. H. *Chem. Commun.* **1966** 740; *Acta Chem. Scand.* **21** (1967) 2289.
2. Misra, R., Pandey, R. C. and Sukh Dev. *Tetrahedron Letters* **1964** 3751; Cocker, W., Moore, A. L. and Pratt, A. C. *Tetrahedron Letters* **1965** 1983; Pinhey, J. T. and Simpson, R. F. *Chem. Commun.* **1967** 9; Jefferies, P. R. and Payne, T. G. *Tetrahedron Letters* **1967** 4777.
3. Fraser, R. R. *Can. J. Chem.* **38** (1960) 549.

Received December 1, 1967.

Benzene-induced Solvent Shifts in the NMR-spectra of Acetophenones and Acetyl Chromenes

THORLEIF ANTHONSEN

*Organic Chemistry Laboratories, Norway
Institute of Technology, Trondheim, Norway*

In the work with chromenes from *Eupatorium* species,¹ we were faced with the problem of differentiating between the structures 1a and 2 for a new chromene isolated from *Eupatorium riparium* Regel, isomeric with evodionol (3a)² and allo-evodionol (4).³ In the following the new chromene is designated ripariochromene.

In a recent communication Scheinmann⁴ has reported that a methoxyl group in xanthenes is shifted 0.6 ppm when going from deuteriochloroform to benzene as solvent. However, the Δ -value [$\Delta = \tau(\text{benzene}) - \tau(\text{CDCl}_3)$] is 0.4 ppm lower