The Diterpenoids of Some *Solidago* Species

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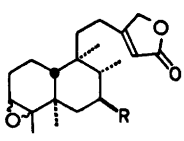
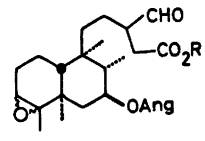
We have continued our studies [1] of the diterpenoids in the genus *Solidago*. From extracts of the roots of *S. Shortii* Torr. & Gray we have isolated two new epoxybutenolides closely related to the elongatolides.[2] The β-substituted $\Delta^{\alpha,\beta}$-butenolide ring is clearly visible in the UV [λ_{max} (EtOH) 226 nm], IR (1780, 1750 cm^{-1}) and NMR [4.16 (H-14), 5.27 (2 H-16) τ] spectra.

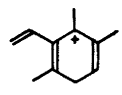
Resonances in the NMR spectrum at 7.11 (1 H *d*, $J = 5$ Hz) and 8.78 (3 H s) are indicative of a trisubstituted epoxy grouping. This together with the presence of two additional tertiary (8.89, 9.06) and one secondary (9.12, $J = 6$ Hz) methyl group shows that the new compounds belong to the clerodane class of rearranged labdanes. One of them (*1*) is not further oxygenated, the other is a secondary angelate (*2*) [IR 1710 cm^{-1}, MS loss of $C_5H_8O_2$, $C_5H_7O^+ \rightarrow C_4H_7^+ + CO$ m* 36.5, NMR 3.96 (1 H qq, $J = 7$ and 1.5 Hz) 8.0 – 8.2 (6 H multiplet)]. The carbinyl proton in the NMR spectrum gives rise to a doublet of triplets centred at τ 5.02 (see Fig. 1) diagnostic of an axial proton coupled to one neighbouring equatorial ($J = 6.0$) and two axial ($J = 10.5$) protons, thus suggesting the oxygen function to be located either at C-1 or C-7. Evidence which lead to choice of the latter was found in the mass spectral process: $C_{25}H_{36}O_5^{\cdot+} \rightarrow C_{20}H_{25}O_3^{\cdot+} \xrightarrow{*} C_{14}H_{21}O^+ \rightarrow C_{11}H_{15}^+$ (*3*). Loss of the epoxy function as C_3H_6O to furnish ion *3* was found to be a more likely process with the oxygen function in ring B.



1 R = H
2 R = OAngeloyl



4 R = H
5 R = Me



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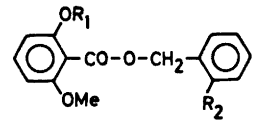
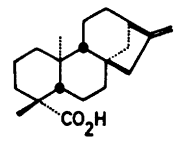


6 R_1 = Me R_2 = H
7 R_1 = H R_2 = OMe



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Hydrolysis (KOH/MeOH, room temp., 12 h) of the angelate furnished an aldehyde acid (*4*) purified on TLC as its methyl ester (*5*) and characterized by its spectroscopic properties [NMR 0.29 (1 H), 6.31 (3 H) $M^{\cdot+}$ $C_{26}H_{40}O_6$].

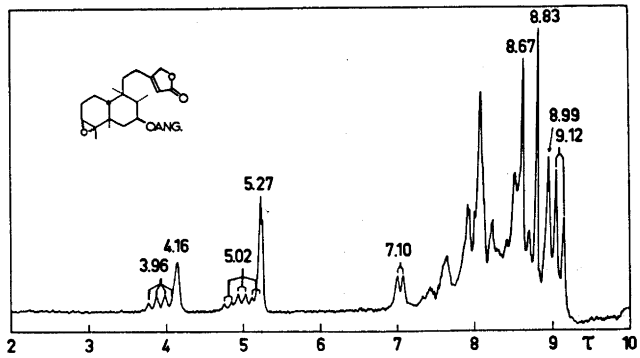

Fig. 1. The NMR spectrum at 60 Mc/s of the butenolide *2*.

Solidago virgaurea L. did not yield any diterpenoids. Besides acetylenic compounds [3] we have found an aromatic ester (*6*) which has been identified by spectroscopic methods [NMR 6.28 (6 H s), 4.72 (2 H s), 3.54 (2 H), 2.84 (1 H) (A_2B, $J = 8.5$ Hz); MS $C_{16}H_{16}O_4^+$· (40 %) → $C_9H_9O_3^+$ (100 %)] and by direct comparison with an authentic sample isolated from *Aster ptarmicoides* Torr. & Gray by Hauge and Sørensen,[4] and also synthesized by the same authors. A related, further oxygenated ester, was isolated from *S. rigida* L. Its spectroscopic properties are similar to those given for an ester (*7*) also found in *Aster ptarmicoides*.[5] However, our m.p. 94–96°C is different from Bohlmann's 35°C. The chemical relationship between the genera *Aster* and *Solidago* is not surprising since they both belong to the tribe Astereae in the Compositae family.

In addition to this, *S. rigida* L gave a diterpenoid acid which is identical with (NMR, MS, IR, TLC) *ent*-16-kauren-19-oic acid (*8*).[6]

We did not succeed in isolating any diterpenoids from *S. flexicaulis* L.; however, four well known acetylenic methyl esters were identified, 2-*trans*,8-*cis*- and 2-*cis*,8-*cis*-matricaria ester and 2-*cis*- and 2-*trans*-dehydromatricaria ester.

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3. Lam, J. *Phytochemistry* **10** (1971) 647.
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Isolation of *ent*-16-Kauren-19-oic Acid and *ent*-16-Kauren-19-ol from *Abrotanella nivigena* Muell.

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The biologically important diterpenoid *ent*-16-kauren-19-oic acid (*1*) has been isolated from a number of natural sources. Originally it was found in *Ricinocarpus stylosus*,[1] but later it has been shown to be present also in *Gibberella fujicuroi*,[2] *Aralia cordata* [3] and, using a bioassay technique, in barley [4] together with the corresponding alcohol *ent*-16-kauren-19-ol (*2*).

The acid and the alcohol which both show gibberellin-like activity,[5] are intermediates in the biosynthesis of the gibberellins [6–9] and they are synthesized in wild cucumber, *Echinocystis macrocarpa*, from kaurene.[10]

We now wish to report the occurrence of these two diterpenoids in the Australian member of the *Compositae* family *Abrotanella nivigena* Muell.

ent-16-Kauren-19-oic acid (*1*) was identified by its physical and spectroscopic properties. Like earlier workers [2] we were, in spite of several recrystallizations, unable to increase the melting point above 160–163° to reach the originally reported [1] value of 179–181°.

The IR spectrum had bands at 1690, 1660, and 875 cm^{-1} due to the carboxylic acid and exocyclic methylene groups. The NMR spectrum exhibited two sharp singlets at τ 9.05 (C-10 Me) and 8.76 (C-4β Me) and three broad signals at τ 5.21 (2H C-17), 7.37 (1H C-13) and 7.91 (2H C-15).

A prominent peak at *m/e* 302 (78 %) in the mass spectrum revealed the presence of a stable molecular ion, the base peak being at *m/e* 91 ($C_7H_7^+$).

A peak at *m/e* 259 (38 %) due to the transition $302^+ \rightarrow 259^+ + 43$ ($\cdot C_3H_7$) has its origin in extrusion of a part of ring A. The presence of the carboxylic acid group is confirmed by the processes $302^+ \rightarrow 257^+ + 45$ ($\cdot CO_2H$) (14 %), $287^+ \rightarrow 241^+ + 46$ (HCO_2H) (21 %) and $259^+ \rightarrow 213^+ + 46$ (HCO_2H) (19 %).