

Solidago virgaurea L. did not yield any diterpenoids. Besides acetylenic compounds³ 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) (A₂B, *J* = 8.5 Hz); MS C₁₆H₁₄O₄⁺. (40 %) → C₈H₆O₃⁺ (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.

Acknowledgements. We want to thank Curator Jan Tengnér, Bergianska Trädgården, Stockholm, for plant material, Dr. Jørgen Lam, Aarhus Universitet, for a copy of his manuscript prior to publication, and Mrs. J. Stene Sørensen, this university, for identifying the acetylenes. This work was supported by a grant from *Norges tekniske høgskole* to G. B., for which we are grateful.

1. Anthonsen, T. and Bergland, G. *Acta Chem. Scand.* **24** (1970) 1860.
2. Anthonsen, T. and McCrindle, R. *Acta Chem. Scand.* **23** (1969) 1068.
3. Lam, J. *Phytochemistry* **10** (1971) 647.
4. Hauge, M. and Sørensen, N. A. *3rd Nordic Natural Product Symposium*, Ørsta, Norway, June 1969.
5. Bohlmann, F., Zdero, C. and Kapteyn, H. *Chem. Ber.* **102** (1969) 1689.
6. Anthonsen, T. and Chantharasakul, S. *Acta Chem. Scand.* **25** (1971) 1925.

Received June 18, 1971.

Isolation of *ent*-16-Kauren-19-oic Acid and *ent*-16-Kauren-19-ol from *Abrotanella nivigena* Muell.

THORLEIF ANTHONSEN and SUPA CHANTHARASAKUL

Institutt for organisk kjemi, Universitetet i Trondheim, Norges tekniske høgskole, Trondheim, Norway

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 barley⁴ 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 gibberellins⁶⁻⁹ and they are synthesized in wild cucumber, *Echinocystis macrocarpa*, from kaurené.¹⁰

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

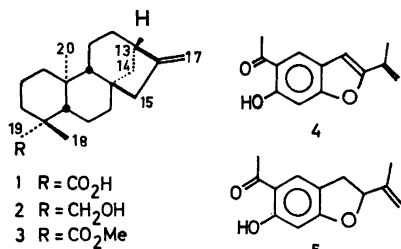
ent-16-Kauren-19-oic acid (1) was identified by its physical and spectroscopic properties. Like earlier workers² we were, in spite of several recrystallizations, unable to increase the melting point above 160–163° to reach the originally reported¹ value of 179–181°.

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 (C₇H₇⁺).

A peak at *m/e* 259 (38 %) due to the transition 302⁺ → 259⁺ + 43 (·C₃H₇) has its origin in extrusion of a part of ring A. The presence of the carboxylic acid group is confirmed by the processes 302⁺ → 257⁺ + 45 (·CO₂H) (14 %), 287⁺ → 241⁺ + 46 (HCO₂H) (21 %) and 259⁺ → 213⁺ + 46 (HCO₂H) (19 %).

ent-16-Kauren-19-ol (2) was isolated from *A. nivigena* as colourless needles, m.p. 135–37°. The IR spectrum had bands at 3380, 1660, and 880 cm^{-1} due to hydroxy and exocyclic methylene groups. The NMR spectrum was similar to the NMR spectrum of kaurenoic acid (1) concerning the signals due to the hydrogens at C-13,



C-15, and C-17; the methyl group resonances, however, were closer together (8.96 and 9.03) and a characteristic AB-quartet ($J=11$ Hz) appeared at τ 6.22 and 6.55 due to the C-19 methylene protons.

The mass spectrum of kaurenol (2) exhibited a strong molecular ion peak at m/e 288 (82%), and the base peak at m/e 257 arises from loss of a methylene-hydroxy radical ($288^{+} \rightarrow 257^{+} + 31$). Loss of C_3H , in this spectrum produces a peak at m/e 245 (13%). Kaurenol (2) was synthesized from kaurenoic acid (1) after LAH reduction of the methyl ester (3).

In addition to the diterpenoids we have isolated euparin (4), a yellow crystalline (m.p. 120°) benzofuran previously known to be present in *Eupatorium* species.¹¹

Chemical investigation of *A. fosteroides* Hook. did not yield any diterpenoids, but considerable amounts of euparin (4) and also a related compound, hydroxytremetone (5) (m.p. 70°). The latter has been found also in *Eupatorium* species, the toxic American "white snakeroot".¹²

Experimental. Spectra were recorded on the following instruments: IR: Perkin Elmer 257, NMR: Varian A-60A, MS: AEI MS 902. The elemental composition of all important peaks in the mass spectra was determined by peak matching. Silica gel for column and thin-layer chromatography was supplied by E. Merck.

Abrotanella nivigena Muell. was collected 1961 at Kosciusko in Snowy Mountains, New South Wales, Australia. The plant material (175 g) was extracted with acetone, evaporated

and chromatographed on a silica gel column. Fraction 4 (20% ether in petroleum ether) yielded after further purification on TLC (twice 20% ether in petroleum ether) 70 mg of 1, 10 mg of 2, and 140 mg of 4. The acid (1), crystallized from methanol $[\alpha]_{\text{D}} = -105^{\circ}$ (CHCl_3) (Calc. for $\text{C}_{20}\text{H}_{30}\text{O}_2$: 302.2245. Found: 302.2227), gave, after methylation with diazomethane and LAH reduction of the methyl ester (3), an alcohol identical (NMR, TLC) with the natural alcohol 2 $[\alpha]_{\text{D}} = -65^{\circ}$ (CHCl_3). (Calc. for $\text{C}_{20}\text{H}_{32}\text{O}$: 288.2453. Found: 288.2459.)

Euparin (4) was isolated as a yellow crystalline compound, m.p. 120° (Calc. for $\text{C}_{13}\text{H}_{12}\text{O}_3$: 216.0786. Found: 216.0788), λ_{max} (EtOH): 263 (35 000), 358 nm (5900). The NMR spectrum contained resonances of one aromatic acetyl methyl group (τ 7.40), one olefinic methyl group (7.93, d, $J=1$ Hz), two well separated, slightly broadened vinylic hydrogens (4.30, 4.88), two aromatic hydrogens [2.23 (C-4), 3.56 (C-7)], one strongly hydrogen bonded hydroxyl hydrogen (-2.43), and the benzofuran hydrogen at C-3 (3.12).

Abrotanella fosteroides Hook. was collected 1961 at Great Lake, Tasmania. After acetone extraction chromatography on silica gel column and TLC none of the above mentioned diterpenoids could be detected, but large amounts of euparin (4) and, as a minor constituent, a colourless crystalline compound, m.p. 70° [λ_{max} (EtOH): 238, 280 and 326 nm] was isolated. This compound (Calc. for $\text{C}_{13}\text{H}_{14}\text{O}_3$: 218.0943. Found: 218.0942) was identified by its IR and NMR spectra as hydroxytremetone (5) [IR (CCl_4): 1635, 1475, 1360, 1317, 1127, 1032 and 902 cm^{-1}]. The NMR spectrum contained signals due to one aromatic acetyl methyl group (τ 7.48), one olefinic methyl group (8.25, d, $J=1$ Hz), two vinylic hydrogens (4.90 and 5.08), two aromatic hydrogens [2.52 (C-4) and 3.63 (C-7)], one strongly hydrogen bonded hydroxyl hydrogen (-2.97), and signals due to the three hydrogens on the dihydrobenzofuran system which forms an ABX pattern [ν_{A} 7.11, ν_{B} 6.67, ν_{X} 4.76, $J_{\text{AX}}=8$, $J_{\text{BX}}=9$, $J_{\text{AB}}=16$ Hz, A and B (C-3), X (C-2)].

Acknowledgements. *Abrotanella nivigena* is an extremely scarce and tiny species of the Compositae. This phytochemical investigation would have been impossible without the kind permission of the Division of Plant Industry, CSIRO, to collect a small sample and the very skilled assistance of Dr. Max Gray and Mr. D. Wimbush who pointed out the locality. We are further grateful to Professor and Mrs. N. A. Sørensen for the crude

extracts put at our disposal. S.C. is grateful to NORAD for a fellowship.

1. Henrick, C. A. and Jefferies, P. R. *Aust. J. Chem.* **17** (1964) 578, 915.
2. Cavell, B. D. and Mac Millan, J. *Phytochemistry* **6** (1967) 1107.
3. Shibata, S., Mihashi, S. and Tanaka, O. *Tetrahedron Letters* **1967** 5241.
4. Petridis, C., Verbeck, R. and Massart, L. *Naturwiss.* **53** (1966) 331.
5. Katsumi, M., Phinney, B. O., Jefferies, P. R. and Henrick, C. A. *Science* **144** (1964) 849.
6. Galt, R. H. B. *J. Chem. Soc.* **1965** 3143.
7. Verbiscar, A. J., Cragg, C., Geissman, T. A. and Phinney, B. O. *Phytochemistry* **6** (1967) 807.
8. Sitton, D., Richmond, A. and Vaadia, Y. *Phytochemistry* **6** (1967) 1101.
9. Graebe, J. A., Dennis, D. T., Upper, C. D. and West, C. A. *J. Biol. Chem.* **240** (1965) 1847.
10. Dennis, D. T. and West, C. A. *J. Biol. Chem.* **242** (1967) 3293.
11. Kamthong, B. and Robertson, A. *J. Chem. Soc.* **1939** 925.
12. De Graw, J. I. and Bonner, W. A. *J. Org. Chem.* **27** (1962) 3917.

Received June 18, 1971.

Synthesis of an α -Bromo- β -lactam, 7-Bromo-8-oxo-1-azabicyclo- [4.2.0]octane, by Carbene Insertion*

NILS GUNNAR JOHANSSON and
BJÖRN AKERMARK

*Department of Organic Chemistry, Royal
Institute of Technology, S-100 44 Stockholm,
Sweden*

For some time we have been searching for methods of synthesizing β -lactams, containing in the α -position an atom or group capable of undergoing transformation under conditions not affecting the β -lactam system. Our attention was directed to the discovery of Seyferth and co-workers, that halomethylphenylmercury compounds readily decompose giving phenylmercury halides and halocarbenes,¹ and we have found that on thermal decomposition (*N*-dibromoacetyl-piperidine)phenylmercury (*I*) gives a mixture consisting of two bromo- β -lactams, A and B, and phenylmercury bromide.

For the β -lactams we propose the structures *2a* and *2b*, respectively. These structures would explain the lability of the β -lactams in acidic and alkaline media and are in agreement with their elemental analysis and spectroscopic properties. The NMR spectra indicated that the coupling constant for the C-4a and C-5 protons of the bromo- β -lactam A was larger than that of the isomer B and the resonance of the C-5 proton of A occurs at lower field than that of B. It has been shown that in 2-azetidinones (e.g. *3*) the coupling constant is larger for the *cis* protons (*3a*) than for the *trans* protons (*3b*) and that the C-3 and C-4 protons of the *cis* isomer absorb at lower field than those of the *trans* isomer.²⁻⁴ Hence A must have the *cis* configuration (*2a*) and B the *trans* configuration (*2b*).

These conclusions were supported by the mass spectra of the bromo- β -lactams. The

* Synthesis of Strained Heterocyclic Rings, Part 2. Publication delayed by request of the authors. Part 1. Åkermark, B., Johansson, N. G. and Sjöberg, B. *Tetrahedron Lett.* **1969** 371.