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DITERPENES OF *HELIANTHUS RIGIDUS* AND *H. SALICIFOLIUS**

WERNER HERZ, SERENGOLAM V. GOVINDAN and KINZO WATANABE

Department of Chemistry, The Florida State University, Tallahassee, FL 32306, U.S.A.

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Key Word Index—*Helianthus rigidus*; *H. salicifolius*; Heliantheae; Compositae; kaurane derivatives; ciliaric acid.

Abstract—The chloroform extract of *Helianthus rigidus* gave ciliaric acid and 16-hydroxy-11-kauren-19-oic acid. *H. salicifolius* furnished these compounds as well as (−)-kauranol.

In the course of a search for sesquiterpene lactones in Heliantheae, we have examined *Helianthus rigidus* (Cas .) Desf. and *H. salicifolius* A. Dietr. The only well-characterized substances found in *H. rigidus* were ciliaric acid (**1**), which has been previously isolated from *H. ciliaris* [1], *J. grosseserratus* [2], *H. laciniatus* [3] and *H. niveus* subsp. *canescens* [4], as well as ent-16β-hydroxy-11-kauren-19-oic acid (**2**) which appeared to be a new compound. *H. salicifolius* also gave no lactones, but yielded compounds **1**, **2** and (−)-kauranol (**3**).

The structure assignment for **2** was based on the empirical formula $C_{20}H_{30}O_3$ (high resolution mass spectrometry), the IR spectrum which indicated the presence of a carboxyl group and NMR spectroscopy. The ^1H NMR spectrum displayed three methyl singlets at δ 0.82, 1.22 and 1.31 characteristic of H-20, H-18 and H-17 of a kauranoic acid containing a 16-hydroxyl group while two mutually coupled signals at 5.90 (*br*, *dd*, $J = 10$, 8 Hz) and 5.52 (*dd*, $J = 10$, 3.7 Hz) indicated the presence of two adjacent vinyl protons which, because of multiplicity had to be located at C-11 and C-12. The proposal was supported by the ^{13}C NMR spectrum which exhibited a singlet at 173.26 (C-19), doublets at 132.86 and 126.04 characteristic of =CH–, a singlet at 81.88 (C-16 carrying-OH) and 16 other signals of the multiplicity and chemical shift expected of the proposed structure (see Experimental).

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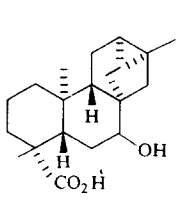
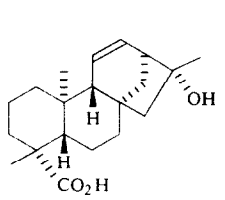
A recent revision [5] of Heiser's infrageneric classification of *Helianthus* spp. [6] places *H. rigidus* in series Atrorubentes and *H. salicifolius* in series Corona-solis of section Divaricati. However, absence of sesquiterpene lactones does not seem to be a characteristic property of the section as defined [5] as is shown by the results on *H. decapetalus* [7], *H. grosseserratus* [2], *H. maximiliani* [8] and *H. mollis* [9]. All of these species are members of series Corona-solis and elaborate sesquiterpene lactones. Heliangin, the first member of the class of heliangolides, was isolated from *H. tuberosus*, also a member of this series, although subsequent workers [7] failed to detect it. Lactones were not reported from *H. giganteus* [7] also in series Corona-solis, and *H. occidentalis* subsp. *plantagineus* [12] in series Atrorubentes. The results on the lactone content of species assigned to other sections [1, 3, 4, 13–16] are also not uniform, although ent-kauranes and trachylobanes are common throughout the genus. Further chemical studies of the genus are clearly needed.

EXPERIMENTAL

Extraction of H. salicifolius. Above ground parts of *H. salicifolius* (9.1 kg), collected by Drs. N. C. Henderson and G. D. Anderson on 20 Sept. 1975 along U.S. Route 50 1.5 miles west of Williamsburg, Franklin Co., Kansas (voucher No. 75–105 on deposit in the Herbarium of the University of Missouri at Kansas City) were extracted with $CHCl_3$ in the usual fashion [17]. The crude gum (75 g) was pre-adsorbed on 115 g Si gel (Mallinckrodt 100 mesh) and chromatographed on 900 g of the same adsorbent packed in toluene–$CHCl_3$ (1:1). Fractions were collected as follows: Fraction 1, toluene–$CHCl_3$(1:1 4 l.); 2–9, $CHCl_3$ (500 ml each); 10–14,



1



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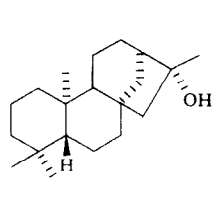

3

MeOH–$CHCl_3$ (1:39, 500 ml each); 15–16 ditto (1 l. each); 17, 18 ditto (500 ml each); 19–21 ditto (800 ml each); 22, 23 ditto (3 l. each) and 24 (MeOH). Fractions 3 and 4, were combined (1.7 g) and purified by TLC (MeOH–$CHCl_3$, 1:24). The major component crystallized on trituration with hexane; further purification by TLC and recrystallization (MeOH–H_2O) resulted in material melting sharply at 142–142.5°, IR ν_{max} 3550 (OH), no carbonyl or double bond frequency, MS *m/z* 290 $[M]^+$, whose ^1H NMR and ^{13}C NMR spectra indicated that it was a mixture of two closely related tetracyclic 16-hydroxylated diterpenes different from (−)-kauranol (**3**). The ^1H NMR spectrum exhibited no frequencies below δ 2.1 and had methyl singlets at 1.32 and 1.28 (minor and major component, H-17), 1.03 and 0.95 (minor and major) 0.85 (major and minor), 0.80 and 0.79 (major and minor).

Fractions 5 and 6 were combined, purified by TLC (MeOH–$CHCl_3$, 1:19) and recrystallized from EtOAc to give 90 mg (−)-kauranol (**3**), mp 214–215°, $[\alpha]_D^{27}$ −46.8° (EtOH; *c* 0.32) [18] IR: OH, no C=O, MS *m/z* 290 $[M]^+$, ^1H NMR: δ 2.0 (H-15a) 1.33 (H-17), 1.00 (H-20) 0.82 and 0.77 (H-18 and H-19). Fractions 16–21 were combined. Repeated fractional crystallization afforded ciliaric acid (**1**) mp 290°, identical in all respects (mp, IR, ^1H NMR and ^{13}C NMR) with material previously isolated from *H. grosseserratus* [2], and ent-16β-hydroxy-11-kauren-19-oic acid (**2**). The latter had mp 240–244° (dec) after recrystallization from EtOAc–EtOH, $[\alpha]_D^{27}$ −250.9° (EtOH; *c* 0.32), ^1H NMR (270 MHz, $CDCl_3$): δ 5.90 (*br dd J*=10, 8 Hz, H-12), 5.52 (*dd*, *J*=10, 3.7 Hz, H-11), 2.15 (*m*, H-15a and H-13), 1.31 (H-17), 1.22 (H-18), 0.82 (H-20); ^1H NMR (C_5D_5N): δ 6.04 (*br t*, H-12), 5.63 (*dd*, H-11), 1.61, 1.41, 1.22 (3 Me), ^{13}C NMR (67.9 MHz, DMSO-d_6); δ 173.26 (*s*, C-19), 132.86 and 126.04 (*d*'s, C-11, C-12), 81.88 (*s*, C-16), 60.77 (*d*, C-13), 58.28 (*t*, C-15), 54.98 (*d*, C-5), 49.28 (*d*, C-9), 42.88 (*s*, C-4), 42.65 (*s*, C-8), 40.91 (*t*, C-1), 39.45 (*t*, C-7), 38.38 (*s*, C-10), 37.60 (*t*, C-3), 33.77 (*t*, C-14), 28.53 (*q*, C-18), 25.68 (*q*, C-17), 21.63 (*t*, C-6), 18.70 (*t*, C-2), 15.33 (*q*, C-20). (Calc. for $C_{20}H_{30}O_3$: MW 318.2195. Found: MW (MS) by peak matching, 318.2203). Other significant peaks in the high resolution MS were at *m/z* (composition, rel. int.) 300 ($C_{20}H_{28}O_2$, 4.8) 285 ($C_{19}H_{25}O_2$, 3.4), 260 ($C_{17}H_{24}O_2$, 65.8), 245 ($C_{16}H_{21}O_2$, 3.8), 242 ($C_{17}H_{22}O$, 4.5), 214 ($C_{16}H_{22}$, 6.2) 199 ($C_{15}H_{19}$, 8.9), 169 ($C_{10}H_{17}O_2$, 12.3), 167 ($C_{10}H_{15}O_2$, 16.6), 159 ($C_{12}H_{15}$, 6.6), 157 ($C_{12}H_{13}$, 5.8), 151 ($C_{10}H_{15}O$, 5.1), 149 ($C_9H_9O_2$, 10.0), 145 ($C_{11}H_{13}$, 30.4), 139 ($C_9H_{15}O$, 8.5), 136 ($C_8H_8O_2$, 27.7), 135 ($C_{10}H_{15}$, 7.2), 135 ($C_9H_{11}O$, 4.5), 91 (C_7H_7, 100).

Extraction of H. rigidus. Above ground parts of *H. rigidus* (10.1 kg), collected by Drs. N. C. Henderson and G. D. Anderson on 20 Sept. 1975 along Interstate 35 1 mile west of the Miami Co. line, Franklin Co., Kansas (voucher No. 75-103) were extracted with $CHCl_3$ and worked up as usual. The crude gum (28 g) was adsorbed on 34 g Si gel and chromatographed on 360 g of the same adsorbent packed in toluene–$CHCl_3$ (1:3). Fractions were collected as follows: Fractions 1–11, $CHCl_3$–toluene (3:1, 400 ml each); 12–14, $CHCl_3$–MeOH (49:1, 600 ml each); 15, $CHCl_3$–MeOH (49:1, 2 l.) and 16, MeOH. Fractions 8–10 (3 g) were combined, trituration with EtOAc afforded crystalline **2** identical with the material from *H. salicifolius*. Fractions 11, 13 and 14 were combined. Trituration with MeOH and recrystallization from $CHCl_3$ gave ciliaric acid, mp 290°.

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