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DITERPENES FROM *SOLIDAGO RUGOSA*

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Key Word Index—*Solidago rugosa*; Asteraceae; Astereae; diterpenes; clerodanes; labdanes; kauranes; *ent*-abietanes.

Abstract—Investigation of the roots and aerial parts of *Solidago rugosa* afforded the known diterpenes kolavenol, hardwickiic acid, (−)-kaur-16-en-19-oic acid, (+)-manool, (+)-3β-hydroxymanool, manoyl oxide and *ent*-abietic acid. In addition, the new labdane diterpene (+)-18-tigloyloxymanool and four new *ent*-abietanes were obtained. The structures of all known and new compounds were elucidated by spectroscopic methods, especially high-field ^{1}H and ^{13}C NMR, and inverse ^{1}H–^{13}C-correlation techniques, as well as chemical transformations. Six diterpenes were tested against *Mycobacterium tuberculosis* and *M. avium*, but showed no significant activities with minimum inhibitory concentrations of $> 100\ \mu g\ ml^{-1}$

INTRODUCTION

In continuation of our search for biologically active compounds from the Asteraceae, we have investigated the roots and aerial parts of *Solidago rugosa* Mill., a member of the large North American genus *Solidago* [1]. Previous studies of this species from the unreported collection site had resulted in the isolation of several diterpene acids and aldehydes [2]. Our investigation provided two known clerodane diterpenes, kolavenol (**1**) [3] and hardwickiic acid (**2**) [4], and four labdane diterpenes (**3**, **4**, **7**, **8**), one of which (**7**) is new. In addition, five abietenes, the known acid **9** and the new analogues **10**–**12** and **14**, as well as kaurenoic acid (**15**) [2] were obtained. The structures of the known and new compounds were elucidated by spectroscopic methods, including MS analysis and high-field ^{1}H and ^{13}C NMR (COSY, NOESY and inverse ^{1}H–^{13}C-correlation methods), as well as chemical transformations.

RESULTS AND DISCUSSION

The structure of **1** was derived by direct comparison with an authentic sample, which had been previously isolated from *S. canadensis* [3] and related taxa [4, 5]. Compound **2**, found before in *Hardwickia pinnata* [4] and *S. juncea* [6], was identified by spectral comparison with reported data. Although the ^{13}C NMR spectrum of the methyl ester of **2** was reported before [7], we performed unambiguous assignments of its ^{13}C NMR spectrum by combined DEPT, COSY and ^{1}H–^{13}C-correlation methods (Table 1). (−)-Kaur-16-en-19-oic acid (**15**), which had been described from several *Solidago* species, including *S. rugosa* [2, 8, 9], exhibited NMR spectral data in accord with published values. Based on the mass spectral analysis, as well as IR, ^{1}H and ^{13}C NMR data, especially COSY, ^{1}H–^{13}C-correlation methods, **3** was identified as (+)-manool [10]. It had been previously found in *Juniperus pseudosabina* [11], *Denekia capensis* [12] and *Viguiera dentata* [13]. (+)-3β-Hydroxymanool (**4**), previously isolated from *J. pseudosabina* [11] and *Gleichenia japonica* [14], exhibited ^{1}H NMR spectral data essentially identical with those reported before [11]. Acetylation products monoacetate **5** and diacetate **6** confirmed the presence of two hydroxyl groups in **4**. The ^{13}C NMR spectra of **4**, and its acetates **5** and **6** were assigned by DEPT and ^{1}H–^{13}C-correlation methods (Table 1). The structure of manoyl oxide (**8**) [15] was derived by mass spectral analysis and direct comparison with previously reported ^{1}H NMR data [16].

Comparison of the ^{1}H NMR spectrum of the new labdane diterpene (**7**) with that of **3** suggested the presence of a tiglate moiety, as indicated by a diagnostic one-proton quartet of a quartet at δ6.82 which was coupled to two broad methyl doublets at δ1.78 and 1.82. This was further supported by its mass spectral data with a prominent peak at m/z 370 $[M-H_2O]^+$. The peaks at m/z 288 and 270 are derived from the loss of tiglic acid $[M-100]^+$ from the parent ion (m/z 388) and m/z 370, respectively. Strong peaks at m/z 83 and 55 further supported the presence of a tiglate side chain. Close inspection of the ^{1}H NMR spectrum of **7** revealed that the tiglate moiety was either attached to C-18 or C-19 (both

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Table 1. ^{13}C NMR spectral data of **2–7**, **9**, **12** and **15** (100 MHz, $CDCl_3$ as internal standard)*

C	**2**	**3**	**4**	**5**	**6**	**7**	**9**	**12**	**15**
1	35.8 *t*	39.1 *t*	37.1 *t*	36.7 *t*	36.6 *t*	38.5 *t*	38.3 *t*	37.7 *t*	41.3 *t*
2	18.2 *t*	19.4 *t*	27.9 *t*	24.3 *t*	24.3 *t*	19.0 *t*	18.1 *t*	18.5 *t*	19.1 *t*
3	140.3 *d*	38.4 *t*	78.9 *t*	80.8 *t*	80.7 *t*	36.5 *t*	37.2 *t*	37.9 *t*	39.7 *t*
4	141.5 *s*	39.5 *s*	39.1 *s*	38.0 *s*	38.0 *s*	37.8 *s*	46.4 *s*	43.6 *s*	43.7 *s*
5	37.6 *s*	55.6 *d*	54.6 *d*	54.7 *d*	54.7 *d*	56.3 *d*	44.9 *d*	49.6 *d*	55.1 *d*
6	38.7 *t*	24.4 *t*	24.0 *t*	23.8 *t*	23.8 *t*	24.5 *t*	25.6 *t*	25.5 *t*	21.8 *t*
7	27.3 *t*	41.4 *t*	38.1 *t*	38.1 *t*	38.0 *t*	38.9 *t*	120.5 *t*	72.5 *t*	40.7 *t*
8	36.3 *d*	145.1 *s*	148.1 *s*	147.9 *s*	147.7 *s*	147.9 *s*	135.6 *s*	149.5 *s*	44.2 *s*
9	38.8 *s*	57.3 *d*	56.9 *d*	56.8 *d*	56.8 *d*	57.4 *d*	51.0 *d*	55.3 *d*	57.1 *d*
10	46.7 *s*	40.0 *s*	39.5 *s*	39.4 *s*	39.3 *s*	40.1 *s*	34.5 *s*	37.4 *s*	39.7 *s*
11	17.5 *t*	17.7 *t*	17.8 *t*	17.8 *t*	17.6 *t*	17.8 *t*	22.5 *t*	20.4 *t*	18.4 *t*
12	27.5 *t*	42.2 *t*	41.2 *t*	41.2 *t*	39.2 *t*	41.3 *t*	27.5 *t*	32.5 *t*	33.1 *t*
13	125.6 *s*	77.2 *s*	73.6 *s*	73.6 *s*	83.3 *s*	73.8 *s*	145.2 *s*	70.8 *s*	43.9 *d*
14	111.0 *d*	145.3 *d*	145.0 *d*	145.1 *d*	141.9 *d*	145.3 *d*	122.5 *d*	124.5 *d*	37.8 *t*
15	142.7 *d*	111.5 *t*	111.7 *t*	111.7 *t*	113.8 *t*	111.6 *t*	34.9 *d*	76.7 *s*	49.0 *t*
16	138.4 *d*	27.7 *q*	28.1 *q*	28.0 *q*	23.5 *q*	27.7 *q*	20.9 *q*	28.8 *q*	155.9 *s*
17	15.9 *q*	106.5 *t*	106.7 *t*	106.9 *t*	107.0 *t*	107.0 *t*	21.4 *q*	28.3 *q*	103.0 *t*
18	172.6 *s*	33.6 *q*	28.3 *q*	28.2 *q*	28.2 *q*	66.7 *t*	185.3 *s*	182.4 *s*	29.0 *q*
19	20.5 *q*	21.7 *q*	15.3 *q*	16.5 *q*	16.5 *q*	27.7 *q*	16.7 *q*	28.0 *q*	183.8 *s*
20	18.3 *q*	14.4 *q*	14.4 *q*	14.5 *q*	14.5 *q*	15.2 *q*	14.0 *q*	13.2 *q*	15.6 *q*
1′				—	—	168.6 *s*	—	—	—
2′	—	—	—	—	—	129.0 *s*	—	—	—
3′				—	—	136.8 *d*	—	—	—
4′				-	—	14.3 *q*	—	—	—
5′	—	—	—	—	—	12.1 *q*	—	—	—
OAc	—	—	—	171.0 *s* 21.3 *q*	171.0 *s*, 21.3 *q*	—	—	—	—
OAc′	—	—	—	—	169.9 *s* 22.2 *q*	—	—	—	—

* Peak multiplicities were determined by heteronuclear multipulse programs (DEPT).

at C-4), since it only showed five methyl signals in the molecule, two of which must belong to the tiglate group and the other two being due to Me-20 (δ0.70) and Me-16 (δ1.27). There were two geminally coupled proton doublets at δ3.88 and 4.29, as shown by COSY and ^{1}H–^{13}C-correlation experiments. Their association with the tiglate ester group was confirmed by 2D inverse long-range ^{1}H–^{13}C-correlation experiment [17] which showed that the two proton signals at δ3.88 and 4.29 coupled to the tiglate carbonyl signal at δ168.6. NOESY experiments revealed that these two proton doublets showed NOEs with Me-20 (δ0.70) while the methyl signal at δ0.99 (C-19) exhibited no NOE with Me-20, indicating that these two methyls were of opposite orientation on the *trans*-decaline ring. Thus, the tiglate side chain must be attached to C-18. The ^{13}C NMR spectrum of **7** indicated the presence of 25 carbons with five methyls, 10 methylenes including two olefinic and one oxygenated carbon, four methines including two olefinic carbons, and six quaternary carbons including one oxygenated, one carbonyl and two olefinic carbons. The total assignments of these carbons were made by DEPT, HOMO- and HETERO-nuclear correlation and inverse long-range ^{1}H–^{13}C-correlation methods (Table 1).

Other diterpenes isolated from *S. rugosa* were *ent*-abietic acid (**9**) [2] and its congeners **10–12** and **14**. Compound **9**, which had been previously isolated from *S. rugosa* [2], exhibited ^{1}H NMR and mass spectral data that were nearly identical with those previously reported [2]. The ^{13}C NMR spectrum of **9** showed the presence of 20 carbons, which were assigned by DEPT and ^{1}H–^{13}C-correlation methods. Unambiguous assignments of four quaternary carbons (C-4, C-10, C-8 and C-13) required the application of 2D inverse long-range ^{1}H–^{13}C-correlations [17, 18]. The methyl proton signal at δ1.25 (H-19) showed correlation to four carbon signals, among these the carbonyl signal at δ185.3 (C-18) and a quaternary carbon signal at δ46.4 which gave the assignment to C-4. The methyl proton signal at δ0.83 (H-20) correlated with the signal at δ34.5 which was assigned to C-10. The two isopropyl methyl proton signals (H-16 and H-17) exhibited a strong cross-peak correlation with the quaternary carbon signal at δ145.2, which was therefore assigned to C-13 and the signal at δ135.6 to C-8.

Compounds **9** and **10** were separated by HPLC, and **10** was shown to be an isomer of the known abietinol [19]. Comparison of ^{1}H NMR data of **10** with those of **9** showed that **10** contained two mutually coupled proton doublets at δ3.15 and 3.37, which were absent in **9**. Furthermore, the upfield shift of the methyl singlet (H-19) from δ1.25 in **9** to δ0.88 in **10** indicated a CH_2OH group in **10** instead of the CO_2H group in **9**. This was further confirmed by a strong IR OH-absorption at 3402 cm^{-1}. The mass spectrum of **10** showed a strong molecular ion peak at *m/z* 288 which is in agreement with the empirical formula $C_{20}H_{32}O$. On biogenetic grounds, **10** must belong to the *ent*-abietinol series, since only *ent*-abietanes have been previously isolated from *Solidago* species, including *S. rugosa* [2, 16].

Compound **11** was identified as the tiglate of **10** since its ^{1}H NMR spectrum clearly showed a one-proton quartet of a quartet at δ6.84 coupled to two broad methyl doublets at δ1.80 and 1.84, which are diagnostic for the tiglate moiety [20]. The only other difference between these two compounds resided in downfield shifts of the two H-18 protons and the methyl group at C-4 (C-19) due to the deshielding effect of the tiglate carbonyl group. The two geminally coupled C-18 protons absorbed at δ4.02 and 4.42 in **11** compared to those at δ3.15 and 3.37 in **10**. The C-4 methyl (C-19) singlet appeared at δ0.99 in **11** and 0.88 in **10**. The mass spectral data of **11** further supported its structure with a prominent molecular ion at *m/z* 370 and strong peaks at *m/z* 287 $[M-83]^+$ and *m/z* 270 $[M-100]^+$, both being derived from the loss of the tiglic acid. Further strong peaks of *m/z* 83 and 55 were also characteristic for the tiglate moiety.

Compound **12**, the most polar diterpene from *S. rugosa* (TLC, $R_f = 0.09$, hexane–Me_2CO, 4:1), showed in its IR spectrum a strong broad absorption at 3500–2500 cm^{-1}, which indicated a carboxylic acid group. Since its methyl ester **13** still gave an IR absorption at 3440 cm^{-1}, the presence of hydroxyl(s) was suggested. This was further supported by the ^{13}C NMR data of **12** which indicated the presence of three oxygenated carbons with one CH-absorption at δ72.5 and two quaternary carbon signals at δ70.8 and 76.7. The ^{13}C NMR spectrum of **12** showed the presence of 20 carbons with only two olefinic carbon signals, one methine at δ124.5 and another quaternary carbon signal at δ149.5, indicating that only one carbon–carbon double bond was present in the molecule. Inspection of the COSY spectrum of **12** revealed that the olefinic proton at δ6.12 (*d*, $J = 1.4$ Hz) only showed allylic coupling to the proton signal at δ4.90. The latter was further coupled to two geminally coupled protons at δ1.16 and 2.27 which were further coupled to a proton signal at δ1.87. All of the above information together with comparison to other analogues from *Solidago* species [6, 16] suggested that **12** was a 7-hydroxy-8-(14)-ene abietic acid with additional functional groups. Instead of the presence of an isopropyl group, as in most other abietanes, the two downfield methyl singlets at δ1.40 and 1.42 (Me-16, Me-17), along with two oxygenated quaternary carbon signals at δ70.8 and 76.7, indicated that in **12** either an epoxide or two hydroxyl groups had to be at positions 13 and 15. The FAB mass spectrum of the methyl ester **13** showed prominent peaks at *m/z* 367 $[M+H]^+$, 365 $[M-H]^+$, 347 $[M-H-H_2O]^+$, 333 $[M-Me-H_2O]^+$, 331 $[MH-2H_2O]^+$, 315 $[M-Me-2H_2O]^+$ and 313 $[MH-3H_2O]^+$. This fact favoured the presence of a diol rather than an epoxide in structure **12**. Although, values up to nearly δ70 can be observed for alkyl-substituted epoxide carbon signals [21], the ^{13}C NMR resonances for C-13 and C-15 at δ70.8 and 76.7, respectively, clearly appear in the range of hydroxyl-bearing carbons. Since lack of material prevented further chemical and spectral investigations to unambiguously exclude an epoxide function between C-13 and C-15, the diol structure **12** is tentatively proposed and the stereochemistry at C-13 remains open. Inspection of a stereomodel of **12** suggested that the hydroxyl at C-7 should be in the axial β-position, since H-7 only showed small couplings ($J = 2.1$, 4.2 Hz) with the two bisecting neighbouring protons at C-6. The ^{13}C NMR spectrum of **12** was assigned by the DEPT, COSY and ^{1}H–^{13}C-correlation methods (Table 1).

The ^{1}H NMR and mass spectral data of **14** were very similar to the reported data of 15-hydroxydehydroabietic acid previously isolated from *Cedrus deodara* [22]. However, based on biogenetic considerations, **14** should also belong to the same enantiomeric series as the other abietanes from *S. rugosa* and related *Solidago* species [2, 16]. Therefore, its stereo-structure must be of the *ent*-15-hydroxydehydroabietic acid, as shown in **14**.

Diterpenes **1**, **2**, **4–6** and **9** were tested against *Mycobacterium tuberculosis* and *M. avium* by a radiorespirometric method [23]. All six compounds exhibited no significant anti-mycobacterial activity with minimum inhibitory concentrations of > 100 μg ml^{-1}.

EXPERIMENTAL

General. ^{1}H and ^{13}C NMR: $CDCl_3$, Brucker AM 400 or Brucker AC 200 spectrometer; IR: film on KBr plates; MS: Hewlett-Packard 5971A GC-MS or TSQ70 FAB mass spectrometer; VLC [24]: silica gel (MN Kieselgel G); prep. TLC: precoated MN Sil-G 25 UV_{254} plates (thickness 0.25 mm); semiprep. HPLC: 10 μ C18 reversed-phase column (250×10 mm, AllTech) coupled to a LDC/Milton Roy CM 4000 multi-solvent delivery system and an ISCO UV detector using a detection wavelength at 230 nm.

Plant material. Roots and aerial parts of *S. rugosa* Mill. were collected on 19 October 1991, in Washington Parish, Louisiana, U.S.A. (voucher No. Fischer-Lu 432; voucher deposited at the Louisiana State University Herbarium).

Extraction and isolation. Freshly dried roots (1.1 kg), flowers (380 g), and stems and leaves (900 g) were soaked separately at room temp. in CH_2Cl_2 for 24 hr, yielding 19, 14 and 18 g of crude extracts, respectively. Crude root extract (7 g) was chromatographed by VLC to give 10 frs of 150 ml each. Further sepn of fr. 5 by semiprep. HPLC ($MeCN$–H_2O 17:3) afforded **1** (4 mg), **2** (27 mg), **7** (5 mg) and **10** (3 mg). VLC sepn of 7 g of the crude flower extract yielded 20 frs of 100 ml each. Repeated prep. TLC (hexane–CH_2Cl_2 9:1) of fr. 2 afforded **8** (2 mg) and **11** (1 mg). Prep. TLC (petrol–CH_2Cl_2 5:1) of fr. 3 gave **11** (2 mg). Further sepn of fr. 4 by prep. HPLC ($MeOH$–H_2O 17:3) provided **9** (4 mg) and **15** (9 mg). Fr. 6 gave **9** (1.65 g) and fr. 7, after prep. HPLC ($MeOH$–H_2O 9:1), yielded **9** (8 mg) and **10** (1 mg). Fr. 12 provided **4** (370 mg) and fr. 13 gave, after repeated prep.

TLC (hexane–Me$_2$CO 3:1), **12** (2 mg) and **14** (2 mg). Comparison by TLC (hexane–EtOAc 4:1) and ^{1}H NMR of the crude extract of leaves and stems with those of flowers and roots showed that in both extracts the terpenoid constituents showed only minor quantitative differences.

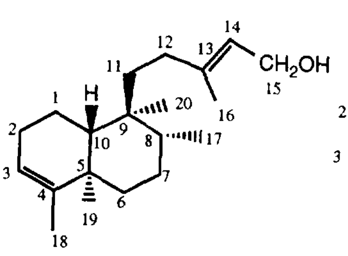
(+)-*3β-Hydroxymanool* (**4**). $C_{20}H_{32}O_2$, gum; IR ν_{max}^{KBr} cm^{-1}: 3402 (OH, br), 1645, 1457 (C = C); EIMS *m/z* (rel. int.): 306 $[M]^+$ (0.1), 288 $[M - H_2O]^+$ (2.8), 273 $[288 - Me]^+$ (10.6), 255 $[273 - H_2O]^+$ (13.1), 135 (100), 43 (68.7); ^{1}H NMR: Table 2; ^{13}C NMR: Table 1.

Acetates **5** *and* **6**. Acetylation of **4** (41 mg) with Ac_2O and 4-dimethylaminopyridine for 16 hr at room temp. after VLC (hexane–Me$_2$CO with increasing polarity), afforded monoacetate **5** (14 mg) and diacetate **6** (5 mg); R_f on TLC (hexane–Me$_2$CO 4:1): **5**:0.57, **6**:0.78.

(+)-*3β-Acetoxymanool* (**5**). $C_{22}H_{36}O_3$, gum; IR ν_{max}^{KBr} cm^{-1}: 3485 (OH, br), 1734 (C = O), 1242 [CC(= O)OC, ester]; EIMS *m/z* (rel. int.): 348 $[M]^+$ (0.1), 330 $[M - H_2O]^+$ (5.1), 315 $[330 - Me]^+$ (7.2), 288 $[M - HOAc]^+$ (3.1), 270 $[330 - HOAc]^+$ (6.3), 255 $[270 - Me]^+$ (28.4), 135 (88.8), 43 $[Ac]^+$ (100); ^{1}H NMR: Table 2; ^{13}C NMR: Table 1.

(+)-*3β,13-Diacetoxymanool* (**6**). $C_{24}H_{38}O_4$, gum; IR ν_{max}^{KBr} cm^{-1}: 1735 (C = O), 1241 [CC(= O)OC, ester]; EIMS *m/z* (rel. int.): 330 $[M - HOAc]^+$ (0.4), 315 $[330 - Me]^+$ (1.5), 270 $[330 - HOAc]^+$ (15.5), 255 $[270 - Me]^+$ (66.5), 135 (100), 43 $[Ac]^+$ (99.3); ^{1}H NMR: Table 2; ^{13}C NMR: Table 1.

(+)-*18-Tigloyloxymanool* (**7**). $C_{25}H_{40}O_3$, gum; IR ν_{max}^{KBr} cm^{-1}: 3496 (OH, br), 1708 (C = O), 1648, 1452 (C = C, conj.), 1263, 1144 (ester); EIMS *m/z* (rel. int.): 370 [M –



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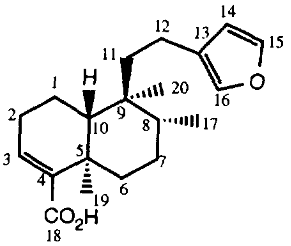

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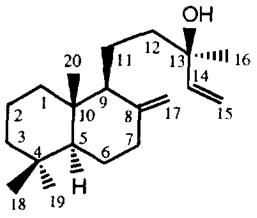

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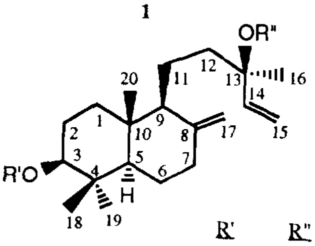
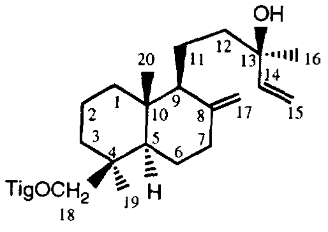


	R'	R"
4	H	H
5	Ac	H
6	Ac	Ac



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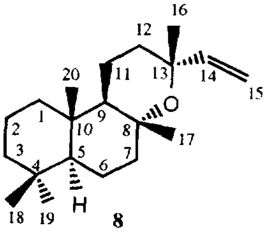

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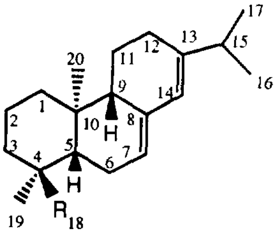
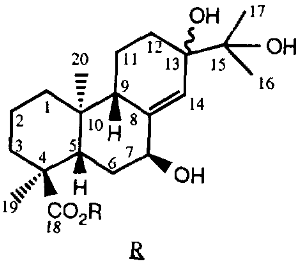
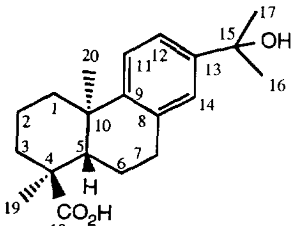


	R
9	-CO_2H
10	-CH_2OH
11	-CH_2OTig



	R
12	H
13	Me



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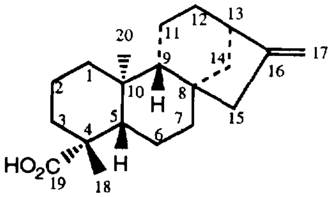

15

$H_2O]^+$ (1.5), 355 $[370 - Me]^+$ (1.3), 288 $[M - MeCH = C(Me)CO_2H]^+$ (1.0), 270 $[370 - MeCH = C(Me)CO_2H]^+$ (12.9), 257 (21.5), 255 $[270 - Me]^+$ (14.3), 135 (43.1), 83 $[MeCH = C(Me)CO]^+$ (100), 55 $[83 - CO]^+$ (40.1); ^{1}H NMR: Table 2; ^{13}C NMR: Table 1.

18-*Hydroxyabieta*-7,13(14)-*diene* (**10**). $C_{20}H_{32}O$, gum; IR ν_{max}^{KBr} cm^{-1}: 3402 (OH, br); EIMS *m/z* (rel. int.): 288 $[M]^+$ (100), 273 $[M-Me]^+$ (11.7), 257 $[M-CH_2OH]^+$ (28.5), 255 $[273-H_2O]^+$ (33.7), 105 (81.1); ^{1}H NMR: Table 3.

18-*Tigloyloxyabieta*-7,13(14)-*diene* (**11**). $C_{25}H_{38}O_2$, gum; IR ν_{max}^{KBr} cm^{-1}: 1717 (C=O), 1265 (conj. ester); EIMS *m/z* (rel. int.): 370 $[M]^+$ (26.5), 287 $[M - 83]^+$ (36.4), 270 $[M - 100]^+$ (74.4), 255 $[270 - Me]^+$ (58.3), 227 $[270 - C_3H_7]^+$ (23.0), 187 (100), 131 (58.2), 83 $[MeCH = C(Me)CO]^+$ (41.8), 55 $[83 - CO]^+$ (46.8); ^{1}H NMR: Table 3.

7-*Hydroxy*-13,15-*dihydroxyabieta*-8(14)-*ene*-18-*oic acid* (**12**). $C_{20}H_{32}O_5$, powder; IR ν_{max}^{KBr} cm^{-1}: 3500–2500 (COOH, br), 1696 (C = O); ^{1}H NMR: Table 3; ^{13}C NMR: Table 1.

Methylation of **12**. Treatment of **12** (3 mg) in 2 ml dry Et_2O with freshly distilled CH_2N_2 in Et_2O provided **13** (~ 3 mg), $C_{21}H_{34}O_5$, powder; IR ν_{max}^{KBr} cm^{-1}: 3440 (OH, br), 1724 (C = O); FAB-MS *m/z*: (rel. int. of signals above $m/z = 300$; m/z $347 = 100\%$): 367 $[M+H]^+$ (5), 366 $[M]^+$ (15), 365 $[M-H]^+$ (52), 349 $[M+H-H_2O]^+$ (16), 348 $[M-H_2O]^+$ (26), 347 $[M-H-H_2O]^+$ (100), 333 $[M-Me-H_2O]^+$ (19), 331 $[M+H-2H_2O]^+$ (61), 330 $[M-2H_2O]^+$ (26), 329 $[M-H-2H_2O]^+$ (91), 313 $[M+H-3H_2O]^+$ (37), 311 $[M-H-3H_2O]^+$ (15); ^{1}H NMR: Table 3.

Table 2. ^{1}H NMR data of **4–7** (400 MHz, in $CDCl_3$)

H	**4**	**5**	**6**	**7**
3	3.24 *dd*	4.52 *dd*	4.50 *dd*	
7α	1.95 *ddd*	1.97 *ddd*	1.96 (overlap)	1.94 *ddd*
7β	2.39 *ddd*	2.39 *ddd*	2.39 *ddd*	2.39 *ddd*
14	5.90 *dd*	5.90 *dd*	5.94 *dd*	5.91 *dd*
15	5.06 *dd* 5.20 *dd*	5.06 *dd* 5.20 *dd*	5.11 *br d* 5.13 *dd*	5.05 *dd* 5.20 *dd*
16	1.27 *s*	1.27 *s*	1.53 *s*	1.27 *s*
17	4.49 *d* 4.82 *d*	4.50 *d* 4.83 *d*	4.51 *d* 4.83 *d*	4.53 *d* 4.82 *d*
18	0.98 *s*	0.87 *s*	0.87 *s*	3.88 *d* 4.29 *d*
19	0.76 *s*	0.84 *s*	0.84 *s*	0.99 *s*
20	0.67 *s*	0.70 *s*	0.70 *s*	0.70 *s*
3′	—	—	—	6.82 *qq*
4′	—	—	—	1.78 *br d*
5′	—	—	—	1.82 *br d*
OAc	—	2.05 *s*	2.05 *s*	—
OAc′	—	—	2.01 *s*	—

J (Hz): **4**: 3, 2α = 4.5; 3, 2β = 11.7; 7α, 7β = 12.8; 7α, 6α = 5.0; 7α, 6β = 12.7; 7β, 6α = 2.5; 7β; 6β = 4.1; 14, 15a = 10.6; 14, 15b = 17.6; 15a, 15b = 1.0; 17a, 17b = 1.0; **5**: 3, 2α = 4.9; 3, 2β = 11.2; 7α, 7β = 12.8; 7α, 6α = 5.0; 7α, 6β = 12.8; 7β, 6α = 2.5; 7β, 6β = 4.1; 14, 15a = 10.7; 14, 15b = 17.3; 15a, 15b = 1.1; 17a, 17b = 1.1; **6**: 3, 2α = 4.2; 3, 2β = 11.8; 7α, 7β = 12.8; 7β, 6α = 2.4; 7β, 6β = 4.1; 14, 15a = 10.9; 14, 15b = 17.5; 17a, 17b = 1.0; **7**: 7α, 7β = 12.7; 7α, 6α = 5.0; 7α, 6β = 12.6; 7β, 6α = 2.4; 7β, 6β = 3.7; 14, 15a = 10.6; 14, 15b = 17.2; 15a, 15b = 1.1; 17a, 17b = 1.0; 18a, 18b = 11.0; 3′, 4′ = 6.8; 3′, 5′ = 1.6.

Table 3. ^{1}H NMR spectral data of **10–14** (400 MHz, *200 MHz, in $CDCl_3$)

H	**10***	**11***	**12**	**13**	**14***
5			1.87 *dd*	1.86 overlap	
6α			1.16 *br dd*	1.16 overlap	
6β			2.27 *ddd*	2.28 *ddd*	
7	5.40 *br s*	5.41 *br d*	4.90 *br dd*	4.90 *br dd*	2.89 *m*
11					7.23 (2H) *d*
12					
14	5.78 *br s*	5.77 *br s*	6.12 *d*	6.11 *d*	7.16 *br s*
15	2.22 *m*	2.23 *m*	—	—	—
16	1.01 *d*	1.01 *d*	1.42 *s*	1.42 *s*	1.56 *s*
17	1.00 *d*	1.00 *d*	1.40 *s*	1.39 *s*	1.56 *s*
18	3.15 *d*	4.02 *d*	—	—	—
18′	3.37 *d*	4.42 *d*	—	—	—
19	0.88 *s*	0.99 *s*	1.28 *s*	1.21 *s*	1.38 *s*
20	0.83 *s*	0.81 *s*	0.46 *s*	0.36 *s*	1.13 *s*
3′	—	6.84 *qq*	—	—	—
4′	—	1.80 *br d*	—	—	—
5′	—	1.84 *br d*	—	—	—
MeO	—	—	—	3.64 *s*	—

J (Hz): **10**: 16, 15 = 17, 15 = 6.8; 18, 18′ = 10.9; **11**: 7, 6α = 2.4; 16, 15 = 17, 15 = 6.7; 18, 18′ = 11.0; 3′, 4′ = 7.0; 3′, 5′ = 1.2; **12**: 5, 6β = 9.5; 5, 6α = 5.4; 6α, 6β = 13.5; 6α, 7 = 2.1; 6β, 7 = 4.2; 14, 7 = 1.4; **13**: 6β, 6α = 13.4; 6β, 5 = 9.2; 6α, 7 = 2.1; 6β, 7 = 4.2; 14, 7 = 1.4; **14**: 11, 14 = 12, 14 = 1.0.

15-*Hydroxydehydroabietic acid* (**14**). $C_{20}H_{28}O_3$, powder; IR ν_{max}^{KBr} cm^{-1}: 3500–2500 (CO_2H, br), 1699 (C=O); EIMS *m/z* (rel. int.): 316 $[M]^+$ (12.2), 301 $[M-Me]^+$ (100), 298 $[M-H_2O]^+$ (15.0), 283 $[301-H_2O]^+$ (45.7), 237 $[283-CO_2H-H]^+$ (64.0), 197 (31.4), 181 (36.4), 43 (63.8); ^{1}H NMR: Table 3.

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