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SESQUITERPENE AND DITERPENE DERIVATIVES FROM *SOLIDAGO* SPECIES*

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Key Word Index - *Solidago odora*; *S. nemoralis*; *S. canadensis*; *S. rugosa*; Compositae; new sesquiterpenes; new diterpenes; new anol derivative; caryophyllene eudesmane, clerodane, labdane, kaurane and abietane derivatives.

Abstract—The investigation of four *Solidago* species afforded, in addition to known compounds, four new caryophyllene derivatives, two eudesmanes, two abietanes, a clerodane, two labdanes, three kauranes and an anol angelate. The structures were elucidated by spectroscopic methods and by some chemical transformations. While the diterpenes isolated are widespread in the genus *Solidago*, the sesquiterpenes have not been obtained before from any species. The overall picture of the large genus, however, is relatively uniform.

INTRODUCTION

From the large American genus *Solidago* (tribe Astereae, family Compositae) fifteen species have been chemically investigated, typical species being clerodane [1–7] and labdane derivatives [8–12]. From some species triterpenes [13, 14], sesquiterpenes [15] and acetylenic compounds [16, 17] were isolated. We have now investigated four further species.

RESULTS AND DISCUSSION

The roots of *S. odora* Ait. afforded the C_{10}-acetylenic esters **1a**, **1b**, **1c**, **2a** and **2b** [16], the phenylpropane derivatives **9**, **10** and **12** together with a new one identified as the angelate **15** from the spectroscopic data. In the ^{1}H NMR spectrum the presence of a symmetric molecule followed from the signal of the aromatic protons (δ 6.59, *s*, 2 H) and the signal of the two methoxy groups (3.83, *s*, 6H), while the vicinal arrangement was indicated by the chemical shift of the 5′-protons (deshielded by the two vicinal methoxy groups). In $CDCl_3$ this signal overlapped with that of the 4′-H, but in C_6D_6 the signals were separated.

The aerial parts of the plant afforded the hydrocarbons **5** and **7**, the phenyl propanes **9** **14** as well as **16**. Only compound **12** has been isolated previously from this plant [18]. The aerial part of *S. nemoralis* Ait. yielded in addition to **5–7**, squalene, phytol, **17a**, **17b**, **18**, **19** (its structure followed from the spectral data, see Experimental), **21** and several derivatives of the latter. The ^{1}H NMR spectrum showed that the main constituent was a benzoate, which also contained an acetoxy group and an epoxide ring (Table 1). In the MS no molecular ion was detected, but chemical ionization with *iso*-butane afforded a clear M + 1 peak (*m/e* 399), which corresponded to the molecular formula $C_{24}H_{30}O_5$. Though no high resolution MS of this peak was possible, the fragments clearly indicated that the proposed formula must be correct. ^{1}H NMR studies including double resonance experiments and the use of shift reagents finally led to the structure **25a**. All signals could be assigned, therefore the stereochemistry also seems to be clear. The observed *W*-coupling of 15-H requires a conformation, which is in good agreement with the observed couplings. Only the configuration at C-4 is uncertain. The model, however, would agree with the given stereochemistry. Partial saponification afforded the hydroxy benzoate **25b**, its ^{1}H NMR spectrum clearly showed that the benzoate residue must be at C-8. In the ^{1}H NMR spectrum of a second compound, which only has the benzoate group (**24**), the chemical shift of 8-H was identical. The ^{1}H NMR data of this second epoxide were very similar to those of **25a** (Table 1). Again this ester showed no molecular ion, but chemical ionization gave a clear M + 1 ion (*m/e* 341) which corresponded to $C_{22}H_{28}O_3$.

Similar caryophyllene derivatives, which must be the precursors of **24** and **25a**, were present in the roots and in the aerial parts in minute amounts. Though the ^{1}H NMR data (Table 1) could not be fully assigned the close relationship is obvious. Also the similarity with the ^{1}H NMR spectrum of **21** supports the proposed structures **22** and **23**.

Finally an abietane derivative was isolated, which most probably was the acetate **28b**. Only the corresponding alcohol **28a** was obtained in a pure state after saponification of the crude acetate. The ^{1}H NMR data (see Experimental) were very similar to those of the corresponding hydrocarbon [20, 21]. The position of the oxygen function could be assigned indirectly only by the Eu(fod)$_3$-induced shifts of the methyl signals. As the oxygen function was obviously tertiary the only possible positions are C-5, C-9 or C-15, only a 5-acetoxy group being in agreement with the shifts observed. Also, the observed *retro*-Diels–Alder fragmentation leading to *m/e* 148 supported this assumption. The stereochemistry at C-5

* Part 277 in the series "Naturally Occurring Terpene Derivatives". For Part 276 see Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19**, 1873.

Me CH=CH [C ≡ C]$_2$ CH=CH CO_2Me

1a	*cis*	*cis*
1b	*cis*	*trans*
1c	*trans*	*trans*

Me[C ≡ C]$_3$CH = CH CO_2 Me

2a	*cis*
2b	*trans*

Ang O CH_2CH = CH[C ≡ C]$_2$CH = CHCO_2Me

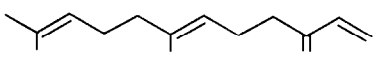
trans *trans*

3

Me[C ≡ C]$_3$[CH = CH]$_2$ $(CH_2)_4$ CH = CH_2

trans

4



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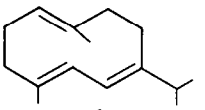

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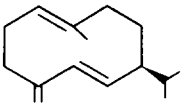

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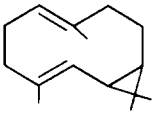

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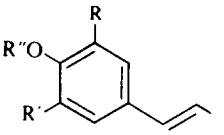
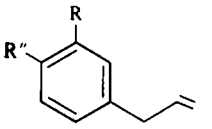
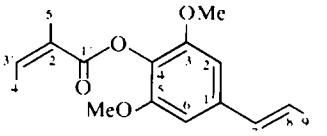


9 R = R' = H, R'' = Me
10 R = R' = OMe, R'' = Me
11 R = H, R' = OMe, R'' = Me
11a R = R' = R'' = H



12 R = H, R' = OMe
13 R = R' = OMe
14 R = H, R' = OH



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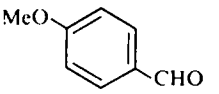

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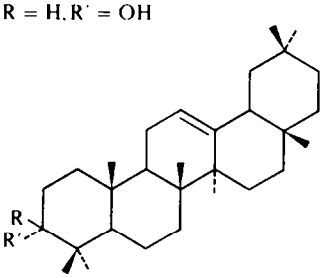
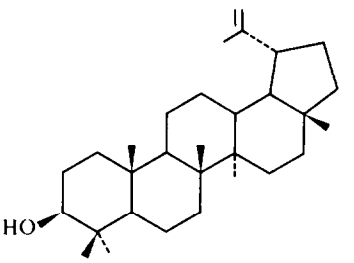


17a R = OH, R' = H
17b R, R' = O



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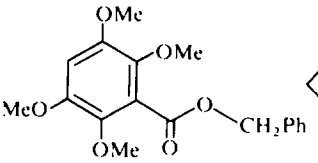

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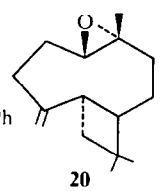

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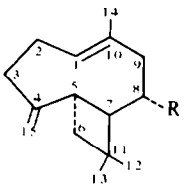
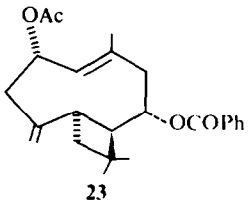


21 R = H
22 R = OCOPh



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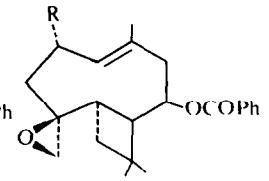
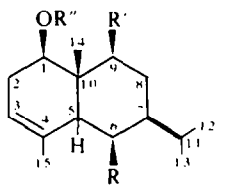
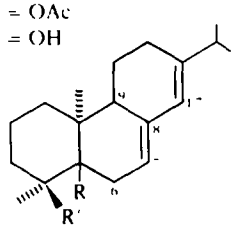


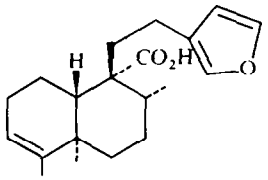
24 R = H
25a R = OAc
25b R = OH





26a R = OCOCH = CHPh, R′ = R″ = H
26b R = OCOCH = CHPh, R′ = R″ = Ac
27a R = H, R′ = OCOCH = CHPh, R″ = H
27b R = H, R′ = OCOCH = CHPh, R″ = Ac

28a R = OH, R′ = Me
28b R = OAc, R′ = Me
29a R = βH, R′ = CO_2H
29b R = βH, R′ = CO_2Me



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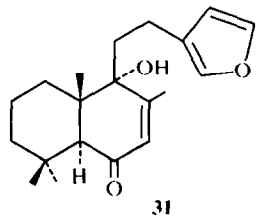

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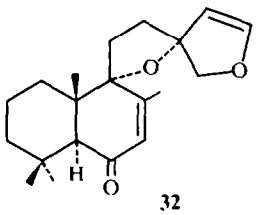

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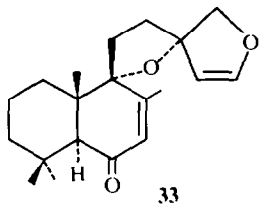

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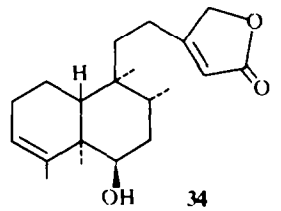

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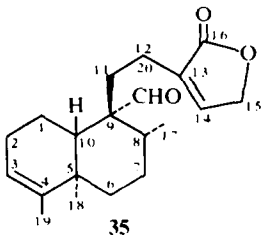

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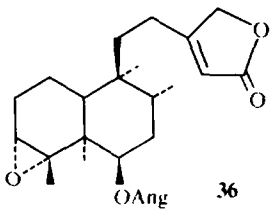

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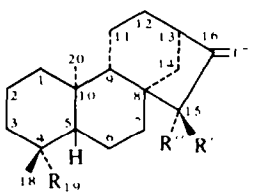
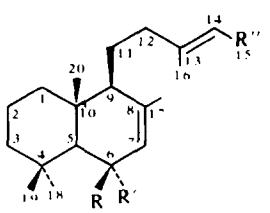


	37	38	39	40	41
R	CO_2H	CHO	CO_2H	CO_2H	CO_2H
R′	H	H	OAng	OSen	OTigl
R″	H	H	H	H	H

	39a	40a	41a	42	43
R	CO_2Me	CO_2Me	CO_2Me	CO_2Me	CO_2Me
R′	OAng	OSen	OTigl	OH	=O
R″	H	H	H	H	



	44	45	46	47
R	OH	=O	OH	=O
R′	H		H	
R″	CH_2OH	CH_2OH	CHO	CHO

Table 1. ^{1}H NMR spectral data of compounds **22**–**25** ($CDCl_3$, 270 MHz, TMS as internal standard)

	22	Δ	**23**	**24**	**25a***	C_6D_6	Δ	**25b**
1-H	5.50 *br. dd*	0.16	5.39 *d(br.)*	5.60 *br. dd*	5.40 *br. dq*	5.16	0.50	5.13 *br. dq*
2-H			5.58 *ddd*		5.61 *ddd*	5.63	1.09	4.66 *ddd*
5-H	2.50 *ddd*		2.49 *ddd*	2.37 *m*	2.54 *br. ddd*	2.27	0.58	2.54 *ddd*
6-H	1.62 *dd*		1.65 *m*	1.6 *m*	1.52 *dd*	1.47	0.44	1.52 *dd*
6′-H	1.7 *m*				1.21 *dd*	1.26	0.72	1.21 *dd*
7-H	2.26 *dd*		2.05 *m*	2.09 *m*	1.84 *dd*	1.66	0.55	1.84 *dd*
8-H	5.22 *ddd*	1.57	5.30 *ddd*	5.22 *ddd*	5.37 *ddd*	5.45	0.62	5.36 *ddd*
9α-H	2.12 *dd*		2.05 *m*	2.16 *dd*	1.70 *dd*	1.47	0.35	1.68 *dd*
9β-H	2.70 *dd*	0.81	2.87 *dd*	2.70 *dd*	3.27 *ddd*	3.28	0.43	3.27 *ddd*
12-H	1.19 *s*	0.26	1.19 *s*	1.10 *s*	1.10 *s*	1.12	0.19	1.10 *s*
13-H	1.00 *s*	0.38	1.00 *s*	0.96 *s*	1.00 *s*	1.00	0.23	1.00 *s*
14-H	1.76 *br. s*	−0.05	1.74 *br. s*	1.83 *br. s*	1.82 *br. s*	1.53	0.31	1.80 *br. s*
15-H	5.07 *br. s*	0.07	5.14 *br. s*	2.76 *d*	2.77 *dd*	2.38	0.87	2.76 *dd*
15′-H	4.94 *br. s*	0.05	5.11 *br. s*		2.73 *d*	2.31	0.94	2.69 *d*
OCOR	8.05 *br. d*	0.61	8.04 *br. d*	8.04 *br. d*	8.03 *br. d*	8.24	0.49	8.03 *br. s*
	7.56 *br. t*	0.07	7.56 *br. t*	7.57 *br. t*	7.57 *br. t*	*m* 7.15	0.19	7.57 *br. t*
	7.45 *br. t*	0.08	7.45 *br. t*	7.45 *br. t*	7.45 *br. t*		0.19	7.45 *br. t*
OAc	—		2.06 *s*	—	2.04 *s*	1.76	0.56	—

* 3α-H 2.24 *br. dd*; 3β-H 1.94 *dd* (C_6D_6: 3α-H 2.11 *dd*, 3β-H 1.97 *dd* (Δ 0.66 and 1.05)).

J (Hz): **22**: 1,2 ~ 9,6; 5,6 = 9; 5,7 = 5; 7,8 = 11; 8,9α = 11; 8,9β = 5; 9α,9β = 11; **23**: 1,2 ~ 10; 2,3 = 10; 2,3′ = 7; **24**: 1,2 = 10; 1,2′ = 8; 5,15 = 2; 7,8 = 11; 8,9α = 11; 8,9β = 5; **25a**: 1,2 = 10; 1,9β = 1.5; 2,3α = 10; 2,3β = 7; 3α,3β = 13; 5,6 = 9; 5,6′ = 10; 5,7 = 10; 5,15 = 1; 6,6′ = 11; 7,8 = 10; 8,9α = 10; 8,9β = 7; 9α,9β = 14; 15,15′ = 4; OCOR: 2′,3′ = 3′,4′ = 8.

cannot be given with certainty and the absolute configuration was not established. As only *ent*-abietanes have been isolated so far from *Solidago* species [11], the given structure is considered more probable.

The roots contained further traces of **4**, the angelate **3**, **21**, **24** and **25a**, and two isomeric eudesmane derivatives, which could be separated only after acetylation. The molecular formula was $C_{26}H_{34}O_4$. The ^{1}H NMR data (Table 2) showed that both were diesters with an acetate and a benzoate residue. Decoupling experiments and comparison with analogous compounds [22] showed that the structures were most probably **26b** and **27b** and consequently the natural compounds should be **26a** and **27a**.

S. canadensis L. has been investigated before by different groups [9, 10, 15] and we have now reinvestigated this species. The roots afforded the hydrocarbons **7** and **8**, the labdanes **31** [9], **32** [10] and **33** [10], the acid **30** [10] and two further labdane derivatives, a diol and a hydroxy ketone, which could be reduced to the diol. All data were in good agreement with the structures **44** and **45**. The *Z*-configuration of the 13,14-double bond followed from the observed chemical shifts of 14- and 16-H, especially after MnO_2-oxidation to the corresponding aldehyde **46** and the ketoaldehyde **47**. The position of the keto group was indicated by the downfield shifts of the signals for 7- and 17-H (Table 3). The other signals were very similar to those of related labdane derivatives [9, 10, 23]. The β-orientation of the 6-hydroxy group followed from the shift differences of the signals for 18- and 20-H in the spectra of **44** and **45**, while the *trans*-annelation of the rings was indicated in the spectrum of **45** by a *W*-coupling (5-H and 20-H) as shown by decoupling. A further *W*-coupling was present between 9- and 17-H (Table 3). The aerial parts afforded **7**, the diterpenes **30**–**33** and caryophyllene epoxide (**20**) [24].

The roots of *S. rugosa* Mill. also contained **7** and the diterpene acids **29a**, **30** [25] and **37**. Compound **29a** must be an isomer of the known abietane derivative with an axial

Table 2. ^{1}H NMR spectral data of compounds **26b** and **27b** ($CDCl_3$, 270 MHz)

	26b	**27b**
1-H	4.77 *dd*	4.87 *dd*
2-H	2.02 *m*	2.0 *m*
2′-H	2.33 *m*	2.48 *m*
3-H	5.34 *m*	5.33 *m*
5-H	2.21 *br. s*	2.0 *m*
6-H	5.75 *br. s*	
9-H		5.32 *dd*
12-H	1.03 *d*	1.00 *d*
13-H	0.86 *d*	0.92 *d*
14-H	1.18 *s*	1.03 *s*
15-H	1.68 *br. s*	1.68 *br. s*
2′-H	6.38 *d*	6.44 *d*
3′-H	7.68 *d*	7.69 *d*
5′,9′-H	7.52 *m*	7.54 *m*
6′,7′,8′-H	7.38 *m*	7.39 *m*
OAc	2.07 *s*	2.06 *s*

J (Hz): **26b**: 1,2 = 11; 1,2′ = 6; 11,12 = 11,13 = 7; 2′,3′ = 16; **27b**: 1,2 = 9.5; 1,2′ = 7; 8α,9 = 5; 8β,9 = 12; 11,12 = 11,13 = 6.

Table 3. ^{1}H NMR spectral data of compounds **35**, **39a**–**47** (270 MHz, $CDCl_3$, TMS as internal standard)

	35	**39a***	**42**	**43**	**44**	**45**	**46**	**47**
3-H	5.23 *br. t*							
7-H					5.58 *br. d*	5.77 *dq*	5.61 *br. s*	5.79 *br. s*
13-H		2.68 *m*	2.67 *m*	3.05 *m*				
14-H	7.16 *t*		1.98 *d*	2.38 *d*	5.43 *tq*	5.46 *tq*	5.90 *br. d*	5.93 *br. d*
15-H	4.79 *br. d*	5.26 *dd*	3.77 *br. s*		4.16 *br. d*	4.19 *br. d*	10.00 *d*	10.02 *d*
16-H				—	1.70 *br. s*	1.72 *br. s*	2.19 *d*	2.22 *d*
17-H	1.07 *d*	4.92 *br. s* 4.87 *br. s*	5.10 *br. s* 4.97 *br. s*	5.94 *br. s* 5.25 *br. s*	1.77 *br. s*	1.94 *dd*	1.77 *br. s*	1.94 *br. s*
18-H	0.94 *s*	1.15 *s*	1.18 *s*	1.20 *s*	1.05 *s*	1.16 *s*	1.05 *s*	1.17 *s*
19-H	1.61 *br. d*				1.31 *s*	1.14 *s*	1.31 *s*	1.14 *s*
20-H	10.00 *s*	0.86 *s*	0.86 *s*	0.91 *s*	1.03 *s*	0.85 *br. s*	1.04 *s*	0.87 *s*

* OAng: 6.12 (*qq*, J = 7, 1 Hz), 2.04 (*dq*, J = 7, 1 Hz), 1.93 (*dq*, J = 1, 1 Hz), **40a**: OSen: 5.78 (*qq*, J = 1.5, 1.5 Hz), 2.20 (*d*, J = 1.5 Hz), 1.93 (*d*, J = 1.5 Hz), 5.20 (*dd*, 15-H), **41a**: OTigl 6.90 (*qq*, J = 7, 1 Hz), 1.83 (*dq*, J = 7, 1 Hz), 1.88 (*dq*, J = 1, 1 Hz), 5.23 (*dd*, 15-H); J (Hz): **35**: 2,3 ~ 3.5; 3,19 ~ 2; 8,17 = 7; 14,15 = 1.5; **39a**–**41a**: 15,17 = 2; 3.63, *s*, OMe; **42**: 3,3′ = 13; 14,14′ = 12; 15,17 = 2; 3.65, *s*, OMe, **43**: 3,3′ = 14, 14,14′ = 12.5, 3.65, *s*, OMe, **44**: 5,6 = 6.8 = 4; 14,15 = 7; 14,16 = 1.5;. 4.37, *br. t*, 6-H, **45**: 7,17 = 7,9 = 9,17 = 1.2; 14,15 = 7; 14,16 = 1; 2.06, *br. s*, 5-H; 2.10, *m*, 9-H; **46**: 14,15 = 8; 14,16 = 1; 4.37, *br. s*, 6-H; **47**: 14,15 = 8; 14,16 = 1.5.

CO_2H group at C-4 [26], as the corresponding methyl ester showed the typical IR band for equatorial esters [27]. Again the absolute configuration was not certain. The two known lactones **34** and **36** [19] and three kaurenic acid derivatives, isolated as their methyl esters, were present, all bearing a 15β-acyloxy residue. The ^{1}H NMR data (Table 3) showed that we were dealing with an angelate, a senecioate and a tiglate. Lithium aluminium hydride reduction afforded an alcohol, which on oxidation led to the known ketone **43** [28]. Therefore the structures of the natural compounds must be assigned as **39**, **40** and **41**. Finally an aldehyde was isolated, which most probably had the structure **35**. The structure could only be deduced by comparison with the spectral data of related compounds. The position of the aldehyde group at C-9, and not at C-5, was indicated by the downfield shift of the methyl doublet, while the chemical shift of 18-H was unchanged in comparison with that of simple clerodanes [10]. We have given the trivial name rugosolide to compound **35**.

The aerial parts contained **7**, **29**, **37**, **38** [29] and again **39**, **40** and **41**. Though the absolute configuration of all the diterpenes could not be established, the observed optical rotations indicated that most probably the given ones are correct.

The overall picture of the constituents of the species investigated showed again that clerodane and labdane derivatives are characteristic of this genus. However, *S. odora* seems to be an exception. Furthermore, acetylenes have been isolated only from a few species. More species need to be investigated to obtain a clear picture of the chemotaxonomy of this genus.

EXPERIMENTAL

^{1}H NMR at 270 MHz, TMS as int. standard; MS at 70 eV; optical rotation, $CHCl_3$. The air-dried plant material was extracted with Et_2O petrol (1:2) and the resulting extracts first separated by CC (Si gel, act. grade II) and further by repeated TLC (Si gel GF 254). The acid fractions were esterified by addition of CH_2N_2 in Et_2O soln. Known compounds were identified by comparison of the IR and ^{1}H NMR spectra with those of authentic compounds.

Solidago odora (*voucher RMK* 7154). Roots (50 g) afforded 3 mg **1a**, 2 mg **1b**, 2 mg **1c**, 1 mg **2a**, 1 mg **2b**, 7 mg **9**, 3 mg **10**, 3 mg **12** and 8 mg **15** (Et_2O-petrol, 1:10), while 100 g of aerial parts yielded 6 mg **5**, 10 mg **7**, 200 mg **9**, 6 mg **10**, 4 mg **11**, 4 mg **11a**, 50 mg **12**, 3 mg **13**, 3 mg **14** and 4 mg **16**.

Solidago nemoralis (*voucher* 78/1198). Roots (35 g) afforded 7 mg **3**, traces of **4**, 38 mg **21**, 2 mg **22** (Et_2O-petrol, 1:4), 25 mg **25a** (Et_2O–petrol, 1:10), 2 mg **24** (Et_2O petrol, 1:4), 4 mg **26a** (Et_2O petrol, 2:1), 2 mg **27a** (Et_2O petrol, 2:1) (**26a** and **27a** were separated after acetylation) and 2 mg **28b** (Et_2O petrol, 1:10), while 100 g aerial parts yielded 2 mg **5**, 12 mg **6**, 30 mg **7**, 20 mg squalene, 20 mg phytol, 5 mg **17a**, 2 mg **17b**, 5 mg **18**, 50 mg **19**, 30 mg **21**, 1 mg **23** (Et_2O-petrol, 1:3), 6 mg **24**, 50 mg **25a** (Et_2O-petrol, 1:10) and 1 mg **28b** (Et_2O petrol, 1:10).

Solidago canadensis *L.* (*voucher* 78/1199). Roots (30 g) afforded 30 mg **7**, 15 mg **8**, 12 mg **30**, 135 mg **31**, 130 mg **32**, 65 mg **33**, 3 mg **44** (Et_2O–petrol, 3:1) and 4 mg **45** (Et_2O–petrol, 3:1), while 120 g aerial parts yielded 70 mg **7**, 2 mg **20**, 13 mg **30**, 3 mg **31**, 8 mg **32** and 4 mg **33**.

Solidago nemoralis (*voucher* 78/1198). Roots (35 g) afforded 12 mg **7**, 1 mg **29a**, 110 mg **30**, 1 mg **34**, 2 mg **35** (Et_2O-petrol, 1:1), 1 mg **36**, 1 mg **37**, and 20 mg **39**, **40** and **41** (3:7:10) (Et_2O–petrol, 3:1), while 110 g aerial parts gave 96 mg **7**, 20 mg **29**, 40 mg **37**, 12 mg **38** and 900 mg **39**–**41** (1:2:3).

3,5-*Dimethoxyanolangelate* (**15**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1650 (PhOCOC=C), 1590 (aromatic). MS *m/e* (rel. int.): 276 (M^+, 0.1) ($C_{16}H_{20}O_4$), 194 (M − O=C=C(Me)CH=CH_2, 0.5), 83 ($C_4H_7CO^+$, 70), 55 (83 − CO, 100). CI (*iso*-butane): 277 (M^+ + 1, 100), 195 (M − angelate, 5). ^{1}H NMR ($CDCl_3$): δ 6.59 (*s*, 6-H), 6.40 (*dq*, J = 16, 1.5 Hz, 7-H), 6.20 (*dq*, J = 6.5 Hz, 8-H), 1.89 (*dd*, J = 6.5, 1.5 Hz, 9-H), 3.83 (*s*, OMe), 6.18 (*m*, 3′-H), 2.07 (*br. s*, 4′,5′-H); (C_6D_6): δ 5.87 (*qq*, J = 7, 1 Hz, 3′-H), 2.15 (*dq*, 4′-H), 2.18 (*dq*, 5′-H).

Benzyl-2,3,5,6-tetramethoxybenzoate (**19**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1735, 1595 ($PhCO_2R$). ^{1}H NMR ($CDCl_3$): δ 3.75 (*s*, 2 × OMe), 3.86 (*s*, 2 × OMe), 5.39 (*s*, 2-H), 7.35 (*m*, 3-H), 7.46 (*br. d*,

2-H) ($OCH_2C_6H_5$), 6.58 (*s*, 4-H). MS *m/e* (rel. int.): 332.126 (M^+, 15) ($C_{18}H_{20}O_6$), 317 (M − Me, 11), 302 (M − CH_2O, 3), 91 ($C_7H_7^+$, 100).

8α-Benzoyloxycaryophyllene (**22**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1715, 1270 (CO_2R), 1610, 1590 (aromatic). MS (CI, *iso*-butane) *m/e* (rel. int.): 325 (M^+ + 1, 1), 203 (M + 1 − $PhCO_2H$, 100).

2α-Acetoxy-8α-benzoyloxycaryophyllene (**23**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (OAc), 1720 (CO_2R). MS (CI, *iso*-butane) *m/e* (rel. int.): 383 (M^+ + 1, 1), 323 (M^+ + 1 − HOAc, 13), 201 (323 − $PhCO_2H$, 100).

8α-Benzoyloxy-4,15-epoxycaryophyllene (**24**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720, 1275 (CO_2R). MS (CI, *iso*-butane) *m/e* (rel. int.): 341 (M^+ + 1, 2.5), 219 (M + 1 − $PhCO_2H$, 100).

2α-Acetoxy-8α-benzoyloxy-4,15-epoxycaryophyllene (**25a**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1715, 1270, 1610, 1590 ($PhCO_2R$), 1735, 1240 (OAc). MS (CI, *iso*-butane) *m/e* (rel. int.): 399 (M^+ + 1, 2.5) ($C_{24}H_{30}O_5$), 339 (M + 1 − HOAc, 35), 277 (M + 1 − $PhCO_2H$, 12), 217 (339 − $PhCO_2H$, 100).

$$[\alpha]_{24}^{\lambda} = \frac{589}{+0.4} \quad \frac{578}{+1.2} \quad \frac{546}{+3.7} \quad \frac{436\,nm}{+15.9} \quad (c = 4.3).$$

To 10 mg **25a** in 1 ml MeOH, 0.5 ml 2 N KOH was added at room temp. After 45 min dil H_2SO_4 was added. TLC of the Et_2O extract afforded 5 mg **25b**, colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1710, 1600, 1585 ($PhCO_2R$). ^1H NMR see Table 1. MS (CI, *iso*-butane) *m/e* (rel. int.): 357 (M^+ + 1, 2) ($C_{22}H_{28}O_4$), 339 (M + 1 − H_2O, 10), 235 (M + 1 − $PhCO_2H$, 78), 217 (235 − H_2O, 100).

1β-Acetoxy-6β-cinnamoyloxy-3,4-dehydroeudesmane (**26b**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1245 (OAc), 1715, 1640 ($PhC{=}CCO_2R$). MS *m/e* (rel. int.): 410.246 (M^+, 1%) ($C_{26}H_{34}O_4$), 350 (M − HOAc, 12), 262 (M − $PhCH{=}CHCO_2H$, 5), 202 (262 − HOAc, 55), 159 (202 − C_3H_7, 81), 131 ($PhCH{=}CHCO^+$, 100), 43 ($MeCO^+$, 48).

1β-Acetoxy-9β-cinnamoyloxy-3,4-dehydroeudesmane (**27b**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740, 1245 (OAc), 1715, 164 ($PhC{=}CCO_2R$). MS *m/e* (rel. int.): 410 (M^+, 0.5) ($C_{26}H_{34}O_4$), 368 (M − ketene, 1), 262 (M − $PhCH{=}CHCO_2H$, 1.5), 202 (262 − HOAc, 38), 159 (202 − C_3H_7, 100), 131 ($PhCH{=}CHCO^+$, 74), 43 ($MeCO^+$, 49).

5-Acetoxyabieta-7,13(14)-diene (**28b**). Impure colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (OAc). MS *m/e* (rel. int.): 330 (M^+, 45) ($C_{22}H_{34}O_2$), 270 (M − HOAc, 8), 255 (270 − Me, 25), 227 (270 − C_3H_7, 28), 148 (20) (RDA), 43 ($MeCO^+$, 100). ^1H NMR ($CDCl_3$): δ 5.45 (*m*, 7-H), 5.80 (*br. s*, 14-H) (0.04),* 1.01 and 1.02 (*d*, 16, 17-H), 1.02 (*s*, 18-H) (0.15),* 0.94 (19-H) (0.15),* 0.89 (*s*, 10-H) (0.15).* 4 mg **28b** were saponified at room temp. (MeOH, KOH). TLC (Et_2O-petrol, 1:3) afforded 2 mg **28a**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH). MS *m/e* (rel. int.): 288.245 (M^+, 100) ($C_{20}H_{32}O$), 273 (M − Me, 14), 270 (M − H_2O, 7), 148.125 ($C_{11}H_{16}^+$, 15) (RDA). ^1H NMR ($CDCl_3$): 5.45 (*m*, 7-H), 5.80 (*br. s*, 14-H), 1.02 and 1.01 (*d*, 16, 17-H), 0.97 (*s*, 18-H), 0.94 (*s*, 19-H), 0.83 (*s*, 20-H).

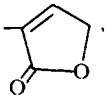
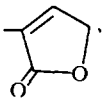
$$[\alpha]_{24}^{\lambda} = \frac{589}{+24} \quad \frac{578}{+28} \quad \frac{546}{+31} \quad \frac{436\,nm}{+51} \quad (c = 0.1).$$

Abieta-7,13(14)-diene-18-oic acid (**29**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2600, 1710 (CO_2H). MS *m/e* (rel. int.): 302 (M^+, 100) ($C_{20}H_{30}O_2$), 287 (M − Me, 15), 259 (M − C_3H_7, 25), 256 (M − HCO_2H, 20). ^1H NMR ($CDCl_3$): δ 5.78 (*br. s*, 13-H), 5.38 (*m*, 7-H), 1.26 (*s*, 19-H), 0.84 (*s*, 20-H), 1.01 and 1.00 (*d*, 16, 17-H, J = 7 Hz).

$$[\alpha]_{24}^{\lambda} = \frac{589}{-25} \quad \frac{578}{-27.5} \quad \frac{546}{-32.5} \quad \frac{436\,nm}{-65.5} \quad (c = 0.2).$$

* $Eu(fod)_3$-induced shifts.

2 mg **29a** were esterified with CH_2N_2 affording 2 mg **29b**, colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730, 1245 (CO_2R, e).

Rugosolide (**35**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (lactone), 1710 (CHO). MS *m/e* (rel. int.): 316.204 (M^+, 14) ($C_{20}H_{28}O_3$), 205 (M − $^{\cdot}CH_2CH_2$–  , 29), 97 ($^+CH_2$–  , 100).

$$[\alpha]_{24}^{\lambda} = \frac{589}{-74} \quad \frac{578}{-80} \quad \frac{546}{-89} \quad \frac{436\,nm}{-153} \quad (c = 0.9).$$

15β-Angeloyloxy-, senecioyloxy- and tiglinoyloxy-ent-kaurenic acid (**39–41**). Colourless gum, which could not be separated, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2600 (CO_2H), 1710 (CO_2H, $C{=}CO_2R$). MS *m/e* (rel. int.): 400 (M^+, 9) ($C_{25}H_{36}O_4$), 300 (M − RCO_2H, 46), 285 (300 − Me, 37), 83 ($C_4H_7CO^+$, 100).

$$[\alpha]_{24^{\circ}}^{\lambda} = \frac{589}{-74} \quad \frac{578}{-80} \quad \frac{546}{-89} \quad \frac{436\,nm}{-153} \quad (c = 0.9).$$

^1H NMR ($CDCl_3$): δ 1.23 (*s*, 18-H), 0.99 (*s*, 20-H), other signals as in **39a–41a** (Table 3). 100 mg **39–41** were esterified in Et_2O with CH_2N_2. TLC (Et_2O–petrol, 1:3) afforded a mixture of **39a 41a**, which again could not be separated, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1725, 1660 ($C{=}CCO_2R$), 1730, 1150 (CO_2R, axial). ^1H NMR: (see Table 3). To 50 mg **39a 41a** in 3 ml Et_2O, 30 mg $LiAlH_4$ were added and after 5 min dil H_2SO was added. The organic layer afforded after evapn and TLC (Et_2O-petrol, 1:1) 25 mg **42** (^1H NMR: see Table 3). 25 mg **42** in 5 ml Et_2O were stirred with 250 mg MnO_2 for 12 hr. TLC (Et_2O–petrol, 1:3) afforded 15 mg **43**, colourless gum, IR and ^1H NMR data identical with those of authentic material.

6β,15-Dihydroxy-ent-labda-7,8,13,14(Z)-diene (**44**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH). MS *m/e* (rel. int.): 306.256 (M^+, 6) ($C_{20}H_{34}O_2$), 291 (M − Me, 8), 288 (M − H_2O, 4), 270 (288 − H_2O, 6), 255 (270 − Me, 15), 43 ($C_3H_7^+$, 100).

$$[\alpha]_{24}^{\lambda} = \frac{589}{-14} \quad \frac{578}{-16} \quad \frac{546}{-17} \quad \frac{436\,nm}{-26} \quad (c = 0.3).$$

3 mg **44** in 3 ml Et_2O were stirred with 30 mg MnO_2 for 12 hr. TLC (Et_2O–petrol, 1:1) afforded 2 mg **46**, colourless gum, ^1H NMR: see Table 3.

15-Hydroxy-ent-labda-7,8,13,14(Z)-dien-6-one (**45**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3630 (OH), 1675 ($C{=}CC{=}O$). MS *m/e* (rel. int.): 304.240 (M^+, 26) ($C_{20}H_{32}O_2$), 289 (M − CH_3, 6), 218 (M − $Me_2C{=}CHCH_2OH$, 67), 95 (C_6H_7O, 100). 3 mg **45** in 1 ml Et_2O were reduced with 20 mg $LiAlH_4$. TLC (Et_2O–petrol, 3:1) afforded 3 mg **44**, identical with the natural diol (IR and ^1H NMR spectra). MnO_2-oxidation of **45** led to **47**, ^1H NMR spectrum: see Table 3.

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