4α-Me), 1 23 (s, 3H, 13β-Me), 3 42 (dd, 1H, J = 8 Hz and 4 Hz, H-3), 3 37 and 4 23 (doublets, J = 10 75 Hz, 4β-$C\underline{H}_2OH$), 4 81 and 4 86 (six lines pattern, 2H, J = 10 5 Hz, 17 5 Hz, 1 5 Hz, $-CH{=}C\underline{H}_2$), 5 71 (dd, 1H, J = 10 5 Hz and 17 5 Hz, $-C\underline{H}{=}CH_2$) ^{13}C NMR ($CDCl_3$, 75 45 MHz) see Table 1

Acknowledgements—We are indebted to Dr A Arnone (Department of Chemistry, Polytechnic School of Milano) for the high resolution NMR spectra This work was supported in part by the "C N R Institute for the Study of Natural Products of Nutritive and Pharmaceutical Interest, Catania"

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Phytochemistry, Vol. 24, No 5, pp 1114–1115, 1985
Printed in Great Britain

0031-9422/85 $3 00 + 0 00

A DITERPENE WITH A NEW CARBON SKELETON FROM *SOLIDAGO ALTISSIMA*

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(*Revised received* 10 *August* 1984)

Key Word Index—*Solidago altissima*, Compositae, diterpenes, new carbon skeleton

Abstract—An Indian sample of *Solidago altissima* afforded in addition to several clerodanes already isolated from other *Solidago* species, a diterpene with a new carbon skeleton Furthermore a ketone and a new anethole derivative were present

Solidago altissima has been studied previously In addition to widespread compounds, several clerodanes were isolated [1] We now have studied a sample collected at Jaipur, India The aerial parts gave 1β-hydroxygermacra-4(15),5,10(14)-triene [2], the known *cis*-clerodane lactones solidago lactone II [1], III [1], V [1] and VII [1] as well as the corresponding tiglate [3]

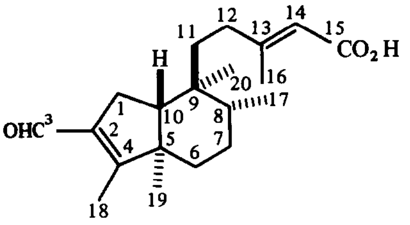
The roots also contain solidago lactone II, III, V, VII and the corresponding tiglate as well as the precursors of the latter two, where the epoxide was replaced by a 3,4-double bond [5] and 2-oxo-kolavenic acid lactone, already prepared from the corresponding alcohol [4] Furthermore the angelate **2**, the *trans*-clerodanes kolavenic acid [5], 7α-acetoxykolavenic acid [6], and 2-oxo-kolavenic acid [7] were present together with the aldehyde **1** The structure of the anethole derivative **2** clearly followed from the spectral data (see Experimental)

The acid **1** was transformed to the methyl ester **1a** The molecular formula was $C_{21}H_{32}O_3$ and the ^{1}H NMR spectral data (see Experimental) indicated the presence of an aldehyde by the singlet at δ9 96 The similarity of several signals with those of methyl kolavenoate showed that most likely these two diterpenes were closely related The presence of a homoallylic coupling between H-18 and H-1 required a five membered ring, especially as by careful spin decoupling all signals and, accordingly, all sequences could be established Therefore kolavenic acid is the precursor of **1**, which may be formed via oxidative cleavage followed by aldol condensation Alternatively a rearrangement of 2-hydroxy-3,4-epoxy kolavenic acid can be considered Compound **1** we have named solidagonal acid

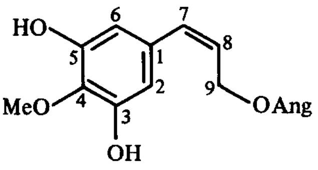
The co-occurrence of *cis*- and *trans*-clerodanes in this species is remarkable In all cases, where a 6-oxygen function is present, the configuration is 9β-methyl and 10αH, while in all other cases *trans*-clerodanes with 10βH and 9α methyl were observed

EXPERIMENTAL

The air dried aerial parts (200 g) and the roots (70 g), collected in the campus of Rajasthan University, Jaipur, India, voucher deposited in RUBL-Herbarium, were extracted with Et_2O–petrol, 1 2, and worked-up in the usual fashion [8] CC fractions of the aerial parts (A) and the roots (R) were as follows 1 (petrol), 2 (Et_2O–petrol, 1 4), 3 (Et_2O–petrol, 1 1) and 4 (Et_2O) Fraction 2A (aerial parts) gave 15 mg 1β-hydroxygermacra-4(15),5,10(14)-triene TLC of 3A (CH_2Cl_2–C_6H_6–Et_2O, 4 4 1) gave 40 mg solidago lactone VII (R_f 0 5), 50 mg of the corresponding tiglate (R_f 0 4) and 10 mg solidago lactone V (R_f 0 7)



1



2

TLC of 4A (same solvents) afforded 10 mg each of solidago lactones II and III (R_f 0 7 and 0 4) Fraction 2R gave 100 mg kolavenic acid TLC of 3R after addition of CH_2N_2 (Et_2O–petrol, 2 3) afforded 5 mg methyl-6β-angeloyloxy- and 10 mg 6β-tigloyloxy-*cis*-kolavenoate (R_f 0 7 and 0 6), 20 mg methyl-7α-acetoxykolavenoate (R_f 0 5) and 5 mg methyl-2-oxo-kolavenoate (R_f 0 4) Repeated TLC of 4R (CH_2Cl_2–C_6H_6–Et_2O, 4 4 1, several developments) gave 2 mg **1** (R_f 0 7), 5 mg solidago lactone VII (R_f 0 6), 6 mg of the corresponding tiglate (R_f 0 5), 4 mg each of the desoxo derivatives of the two latter (R_f 0 4 and 0 3), 2 mg solidago lactone V and 5 mg 2-oxo-kolavenic acid lactone (R_f 0 15) The identities of the known compounds were established by direct comparison or if material and sufficient data were not available, by extensive ^{1}H NMR studies including NOE difference spectroscopy which allowed the assignment of the stereochemistry

Solidagonal acid methyl ester (**1a**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1720 (CHO, CO_2R), 1665, 1645 (C=C), MS m/z (rel int) 332 235 $[M]^+$ (24) (calc for $C_{21}H_{32}O_3$ 332 235), 317 $[M-Me]^+$ (9), 301 $[M-OMe]^+$ (10), 300 $[M-MeOH]^+$ (12), 285 $[300-Me]^+$ (20), 205 $[M-CH_2CH_2C(Me){=}CHCO_2Me]^+$ (40), 95 (100); $[\alpha]_D$ -111 ($CHCl_3$, *c* 0 15), ^{1}H NMR ($CDCl_3$, 400 MHz, TMS as internal standard): δ2 33 *br dd* (H-1), 2.17 *ddq* (H-1′), 9 96 *s* (H-3), 1 65 *ddd* (H-6), 1 35 *m* (H-6′), 1 55 *m* (H-7), 1 45 *ddq* (H-8), 1 56 *dd* (H-10), 1 40 *m* (H-11), 2 05 *ddd* (H-12), 1 96 *ddd* (H-12′), 5 66 *tq* (H-14), 2 15 *d* (H-16), 0 81 *d* (H-17), 2 02 *dd* (H-18), 0 92 *s* (H-19), 0 85 *s* (H-20), 3 68 *s* (OMe), (*J* [Hz] 1, 1′ = 15, 1, 10 = 7, 1′, 10 = 10, 1, 18 ~ 1, 1′, 18 = 2, 6, 6′ = 12 5, 6, 7 = 6, 7′ = 3, 7, 8 = 10, 7′, 8 = 4, 8, 17 = 7, 11, 12 = 13, 11, 12′ = 6, 11′, 12 = 5 5, 11′, 12′ = 12, 12, 14 = 14, 16 = 1, 12, 12′ = 13)

3,5-Dihydroxy-9-angeloyloxy-cis-anethole (**2**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1720, 1650 (C=CCO_2R), CIMS (isobutane) m/z (rel int) 279 $[M+1]^+$ (100) (corr to $C_{15}H_{18}O_5+1$), ^{1}H NMR ($CDCl_3$): δ6 20 *s* (H-2, H-6), 5 79 *dt* (H-7, *J* = 11, 1 Hz), 6 21 *dt* (H-8, *J* = 11, 6 5 Hz), 4 91 *dd* (H-9, *J* = 6 5, 1 Hz), 3 79 *s* (OMe), 6 10 *qq*, 1 99 *dq* and 1 90 *dq* (OAng)

Acknowledgement—R K S thanks the C S I R, New Delhi, for providing a Junior Research Fellowship

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