Diterpenoids of *Solidago Arguta* Ait. The Stereochemistry of *cis*-Clerodanes

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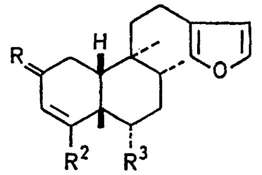
Summary Six new diterpenoids from *Solidago arguta* are formulated as (**1**)—(**6**) on the basis of chemical and spectroscopic evidence and comment is made on the stereochemistry of several related, known, *cis*-clerodanes.

WE have isolated from the roots of *Solidago arguta* Ait. six new diterpenoids (**1**)—(**6**) based on a *cis*-clerodane skeleton and surprisingly, from the same tissue, the known[1] *trans*-clerodane (**7**).

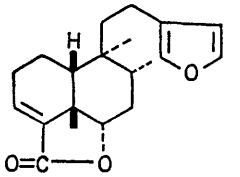
Four of the compounds,‡ (**1**), (**2**), (**3**), and (**4**), $[\alpha]_{\mathrm{D}}$ + 33°, + 49°, + 42°, and + 13° respectively, were obtained as oils and the other two in crystalline form (**5**) m.p. 142—

‡ Satisfactory analytical and spectral data have been obtained for all new compounds.

143°, and (**6**) m.p. 103—104°. The gross structures of all six were deduced from their spectral properties and a series of interconversions and the presence of an A–B *cis*-ring fusion was suggested[2] by the n.m.r. spectrum of the derived αβ-unsaturated ketone (**8**). Reinforcing evidence for the *cis* ring fusion and an indication of the relative stereochemistry at C(5), C(6), C(8), C(9), and C(10) in (**1**) and its congeners came from a study of Eu(dpm)$_3$ induced shifts of the methyl resonances of the alcohol (**9**). The normalised[3] ratio of 10 : 9·6 : 1·7 : 4·2 for the C(4), C(5), C(8), and C(9) methyl groups respectively is consistent only with the relative stereochemistry of (**9**) and a steroid-like[4] conformation of the A–B decalin system.



	R¹	R²	R³
(1)	H_2	Me	H
(2)	H_2	CH_2OAc	H
(3)	H_2	CH_2OH	H
(4)	H_2	CH_2OAc	OH
(6)	H_2	CH_2OH	OH
(8)	O	Me	H
(9)	H_2	Me	OH



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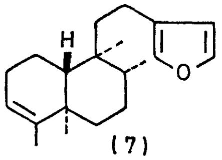

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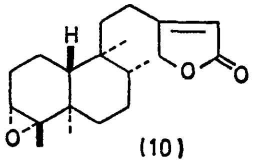

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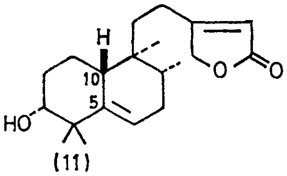

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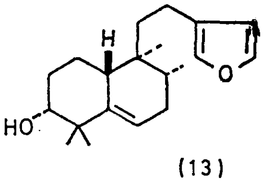
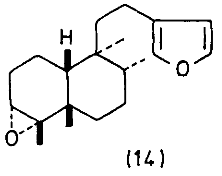
(12) $\Delta^{5,10}$-isomer



(13)

Confirmation of the absolute configuration was achieved chemically. Epoxide (**10**), which has been interrelated[5] with (**7**) of well defined structure,[1] on exposure to BF$_3$ gave a mixture of (**11**) and (**12**). The former, on treatment with di-isobutyl aluminium hydride, gave the alcohol (**13**), $[\alpha]_D$ −33°. Compound (**13**) was also the major product when the epoxide (**14**), derived from (**1**), was treated with BF$_3$. Compounds (**1**) and (**7**) are thus identical except in configuration at C(5).

Elucidation of the absolute stereochemistry of these diterpenoids from *S. arguta* also removes problems concerning the configuration of related *cis*-clerodanes. The observation that the αβ-unsaturated ketone (**8**) and the derivative (**15**) of cistodioic acid[4] have positive Cotton effects of very similar molecular amplitudes (*ca.* +65) implies that cistodioic acid may be formulated as (**16**). Haplopappic acid[6] must then be (**17**) since its reduction to cistodioic acid has been reported. The authors, however, do not comment on the fact that hydrogenation of (**17**) would be expected to produce a mixture of (**16**) and its C(13) epimer. In addition if the provisional stereochemistry (**18**) assigned[7] to marrubiaside is correct, then reduction of a suitable derivative with di-isobutyl aluminium hydride should yield (**3**).§ Finally, the fact that the enones (**19**) and (**20**), derived from solidagoic acid A (**21**)[2] and plathyterpol (**22**)[8] respectively, show negative Cotton effects (*a ca.* −35) associated with the R-band while that of (**8**) is positive adds further weight[2] for the absolute stereochemistry assigned to them.



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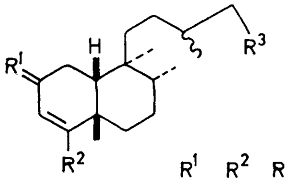
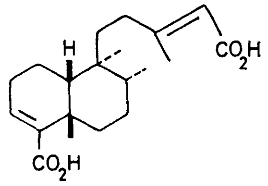


	R¹	R²	R³
(15)	O	Me	Me
(16)	H_2	CO_2H	CO_2H



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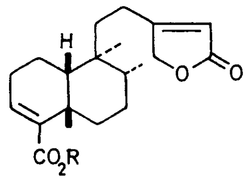
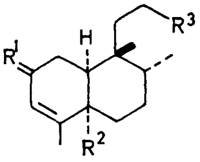
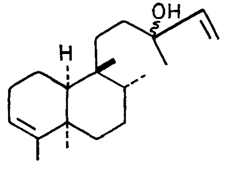


(18) R, β-D-glucopyranosyl



	R¹	R²	R³
(19)	O	Me	Fu
(20)	O	Me	CH_2Me
(21)	H_2	CO_2H	Fu



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§ This transformation will be attempted in collaboration with Professor R. Tschesche.

[1] M. S. Henderson, R. D. H. Murray, R. McCrindle, and D. McMaster, *Canad. J. Chem.*, 1973, **51**, 1322.

[2] T. Anthonsen, M. S. Henderson, A. Martin, R. D. H. Murray, R. McCrindle, and D. McMaster, *Canad. J. Chem.*, 1973, **51**, 1332.

[3] D. G. Buckley, G. H. Green, E. Ritchie, and W. C. Taylor, *Chem. and Ind.*, 1971, 298.

[4] G. Berti, O. Livi, and D. Segnini, *Tetrahedron Letters*, 1970, 1401.

[5] R. McCrindle and E. Nakamura, *Canad. J. Chem.*, in press.

[6] M. Silva and P. G. Sammes, *Phytochemistry*, 1973, **12**, 1755.

[7] R. Tschesche and H.-U. Plenio, *Chem. Ber.*, 1973, **106**, 2929.

[8] T. J. King, S. Rodrigo, and S. C. Wallwork, *Chem. Comm.*, 1969, 683.