Constituents of *Solidago* Species. Part VII.[1] Constitution and Stereochemistry of the *cis*-Clerodanes from *Solidago arguta* Ait. and of Related Diterpenoids

By **Robert McCrindle** * and **Etsu Nakamura**, Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada

Allan B. Anderson, Department of Botany and Genetics, University of Guelph, Guelph, Ontario, Canada

Six new diterpenoids, (2a—e) and (4), with a *cis*-clerodane skeleton and the known *trans*-clerodane (1) have been isolated from the roots of *Solidago arguta*. The constitution and stereochemistry of the new compounds are deduced from their spectral properties, a series of interconversions, and the observation that (2a) and the epoxide (13), of well defined structure, can be transformed into the same derivative (14a). The stereochemistry assigned to marrubiaside (27a) has been confirmed by reducing the related ester (27b) to (2c). Comment is made on the stereochemistry of several related, known, clerodanes, including those from *S. shortii*.

We have isolated one known and six new neutral furyl diterpenoids and two known triterpenoid acids from an ethereal extract of ground, dry roots of *Solidago arguta* Ait.† These constituents are discussed in a sequence based on chromatographic polarity on silica gel, least polar first.

From the least polar fractions, two isomeric furyl olefins were obtained and were readily separated by preparative t.l.c. on silver nitrate–silica gel. The more polar compound (1) was identical with the furyl olefin isolated [1] from a variety of *Solidago serotina*. The n.m.r. spectrum of the less polar isomer (2a) appeared to indicate that it has the same gross structure as (1) and the related *cis*-clerodane (3a) [2] although the n.m.r. spectra and t.l.c. mobilities, on silver nitrate–silica gel, of all three are different. Proof that (2a) differs from (1) only in configuration at C-5 is presented below.

The next constituent (2b) was readily recognised as a close relative of (2a) on the basis of its n.m.r. and i.r. spectra. The former spectrum provided two particularly valuable pieces of structural evidence. First, the chemical shifts attributed to the C-8 and -9 methyl groups closely parallel those of (2a) rather than those of (1). Secondly, resonances for a vinylic CH$_2$·OAc group are evident. As expected, hydrogenolysis of the acetate in the presence of triethylamine gave the furyl olefin (2a).

The corresponding alcohol (2c) was obtained next. Its n.m.r. spectrum is almost identical with that of (2b) except that resonances attributable to CH$_2$·OH replace those for CH$_2$·OAc. Treatment of (2c) with acetic anhydride–pyridine gave the acetate (2b), identical with the compound of natural provenance.

The major constituent, the lactone (4), was obtained in crystalline form. Its n.m.r. spectrum again indicates the presence of a β-substituted furan ring, and a narrow multiplet at τ 3.27 can be attributed to a vinylic proton on a double bond conjugated with a carbonyl group. The i.r. absorption at 1 750 cm^{-1} indicates that this conjugated carbonyl group is not ketonic but probably γ-lactonic in nature. Also present in the n.m.r. spectrum are signals attributable to one secondary and two tertiary methyl groups, in addition to a doublet of doublets at τ 5.78 (1 H) which collapses to a doublet when irradiated at either τ 8.24 or 8.80, suggesting the presence of the

·O·C*H*·CH$_2$· system. From these spectroscopic data and the mass spectrum, the tentative structure (4) was
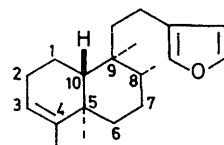
(1)
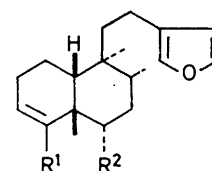
	R^1	R^2
(2) a;	Me	H
b;	CH$_2$·OAc	H
c;	CH$_2$OH	H
d;	CH$_2$·OH	OH
e;	CH$_2$·OAc	OH
f;	CH$_2$·OAc	OAc
g;	Me	OH
h;	Me	OAc
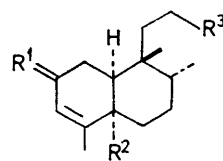
	R^1	R^2	R^3
(3) a;	H$_2$	Me	3-furyl
b;	O	Me	3-furyl
c;	O	Me	Et
d;	H$_2$	CO$_2$H	3-furyl
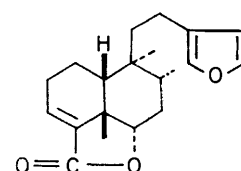
(4)

assigned. The assignment was confirmed by the series of chemical transformations outlined below.

Reduction of the lactone (4) with di-isobutylaluminium hydride at low temperature afforded the diol (2d). Reduction of the lactone with lithium aluminium hydride even at —70 °C gave a mixture of products, the n.m.r. spectrum of which indicated total loss of the 3,4-double bond. Mild acetylation of the diol (2d) yielded a mixture of the monoacetate (2e) and the diacetate (2f). The former, upon hydrogenolysis, afforded the mono-ol (2g), which was also obtained from the diacetate (2f) by hydrogenolysis and then reduction of the resulting mono-

[1] Part VI, R. McCrindle and E. Nakamura, *Canad. J. Chem.*, 1974, **52**, 2029.

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

acetate (2h) with lithium aluminium hydride. A study of the Eu(dpm)$_3$-induced shifts of the methyl resonances of this alcohol (2g) gave unambiguous evidence for the structure, relative configuration, and conformation of the molecule. The normalised ratio [3] of 10 : 9.6 : 1.7 : 4.2 for the shifts of the C-4, -5, -8, and -9 methyl groups, respectively, is consistent only with the presence of a 6-hydroxy-group and with the relative configuration and steroid-like conformation [2] drawn (5).

Oxidation of the alcohol (2g) with Collins' reagent [4] gave the corresponding ketone (6). The magnitudes (see

(5)≡(2g)   (6)
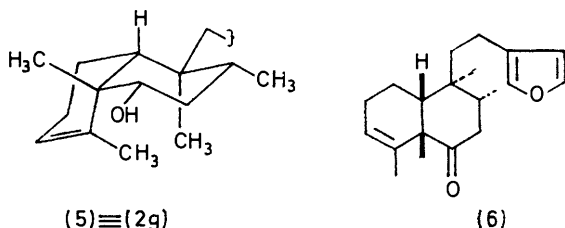
Experimental section) of the benzene-induced shifts in the n.m.r. spectrum of this compound confirm [5] the presence of a ketone at C-6 and again suggest a steroid-like conformation for the molecule. As expected, Wolff–Kishner reduction of the ketone (6) afforded a furyl olefin identical with the natural product (2a).

The next two constituents, the diol (2d) and the mono-acetate (2e) are closely related to the lactone (4). The monoacetate (2e) has i.r. absorptions and n.m.r. signals attributable to an acetate and a hydroxy-group. Significantly, a narrow multiplet at τ 5.18 indicates the presence of the ·CH:C·CH$_2$·OAc system and allowed the assignment of the tentative structure (2e) to this compound, which was then found to be identical with that prepared from the lactone (4).

The most polar diterpenoid constituent is the crystalline diol (2d), which was correlated with the lactone (4) in two ways. As mentioned above, reduction of (4) with di-isobutylaluminium hydride yielded (2d). Furthermore, oxidation of (2d) with Collins' reagent [4] gave (4).

From acidic fractions of the extract after treatment with diazomethane two known triterpenoids were isolated as methyl esters. Oleanolic acid (7a) is the most abundant terpenoid constituent of *S. arguta* roots. Its ester was identified by direct comparison with an authen-

tic sample. Oleanonic acid (7b) is a slightly less abundant constituent. It was also identified as its ester by direct comparison with an authentic sample.

Stereochemistry of the New cis-*Clerodanes.*—Since the gross structures of all six new cis-clerodanes had been tentatively assigned on the basis of their spectral properties and a series of interconversions, the major problem remaining involved the deduction of their relative and absolute configuration. For the simplest of these, the furyl olefin (2a), there are sixteen possible stereochemical variations of the gross structure (8a), since there are four asymmetric centres in the octalin system. Of these sixteen furyl olefins, two [(1) and (3a)] have been reported [1,2] previously,* and we sought the means whereby our new isomer (2a) could be correlated with one of these.

A basis for such a correlation appeared to rest on the fact that rearrangement of the Δ³-clerodenes (8a) to the related Δ^{5,6}-olefins (9a) and Δ^{5,10}-olefins (9b) reduces the stereochemical complexity in a stepwise fashion from the possible eight pairs of enantiomers to four and two pairs, respectively. Indeed, we have devised a system based

(7a)   R
(7b) 3-ketone   (8) a; H$_2$
                                              b; O

(9a)
(9b) Δ^{5,10}-isomer
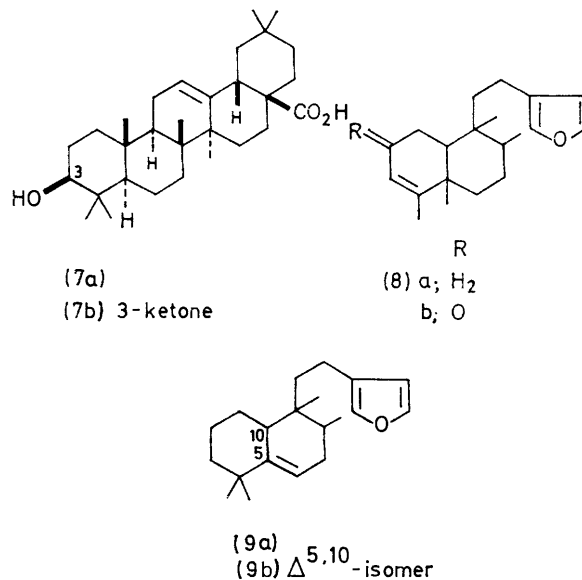
on this concept which should allow complete stereochemical assignment to any † furyl olefin of gross structure (8a).

[7] G. Ferguson, W. C. Marsh, R. McCrindle, and E. Nakamura, *J.C.S. Chem. Comm.*, 1975, 299.

[8] G. Berti, O. Livi, and D. Segnini, *Tetrahedron Letters*, 1970, 1401; C. Tabacik and M. Bard, *Phytochemistry*, 1971, **10**, 3093.

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

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

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

[12] I. Kitagawa, M. Yoshihara, T. Tani, and I. Yosioka, *Tetrahedron Letters*, 1975, 23.

[13] K. K. Cheung, D. Melville, K. H. Overton, J. M. Robertson, and G. A. Sim, *J. Chem. Soc. (B)*, 1966, 853.

[14] T. Okazaki, A. Ohsuka, and M. Kotake, *J. Chem. Soc. Japan*, 1973, 584.

[15] S. Kusumoto, T. Okazaki, A. Ohsuka, and M. Kotake, *Bull. Chem. Soc. Japan*, 1969, **42**, 812; R. Misra and S. Dev, *Tetrahedron Letters*, 1968, 2685.

* A survey of all known clerodanes reveals that variously oxygenated representatives of five of the sixteen possible backbone variations have been isolated.[1,2,6]

† Other common side-chains in natural clerodanes which have been converted into the furan-containing type are those with a terminal butenolide [14] or αβ-unsaturated carboxylic acid.[15]

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

[4] J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Letters*, 1968, 3363.

[5] J. D. Connolly and R. McCrindle, *Chem. and Ind.*, 1965, 379; D. H. Williams and N. S. Bhacca, *Tetrahedron*, 1965, **21**, 2021.

[6] For further leading references see 7—13 and D. Billet, M. Durgeat, S. Heitz, and A. Ahond, *Tetrahedron Letters*, 1975, 3825; S. Hosozawa, N. Kato, and K. Munakata, *Phytochemistry*, 1974, **13**, 1019; W. B. T. Cruse, M. N. G. James, A. A. Al-Shamma, J. K. Beal, and R. W. Doskotch, *Chem. Comm.*, 1971, 1278; L. Brehm, O. J. R. Hodder, and T. G. Halsall, *J. Chem. Soc. (C)*, 1971, 2529.

The two furyl olefins (1) [1] and (3a) [2] were available to us, and we have now prepared the related rearranged ketones (10a), (10b), (11a), and (11b) (see below). Armed with these six reference compounds one is in a position to deal with any given diastereoisomer of gross structure (8a) but of unknown stereochemistry. For the sixteen stereochemical possibilities, three distinct situations may be delineated. First, the furyl olefin may be identical with or antipodal to one or other of the standard furyl olefins (1) and (3a). This eliminates four of the sixteen possibilities. Secondly, this furyl olefin does not match either standard, but the $\Delta^{5,6}$-olefinic ketone derived from it is identical with or antipodal to (10a) or (11a). From this information the stereochemistry of the new furyl olefin at all four chiral centres can be deduced readily. This eliminates a further four possibilities. Thirdly, if neither the new furyl olefin nor the derived
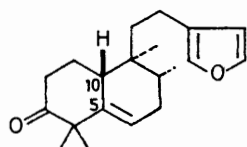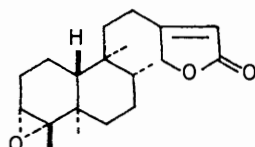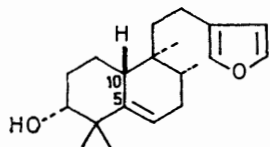

(10a)
(10b) $\Delta^{5,10}$- isomer
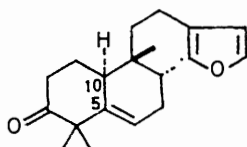
(11a)
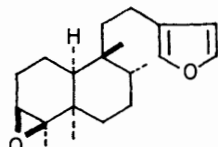(11b) $\Delta^{5,10}$- isomer
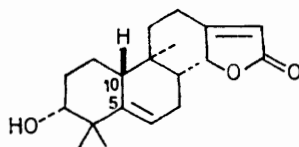
(12a)
(12b) $\Delta^{5,10}$-isomer

(13)

(14a)
(14b) $\Delta^{5,10}$- isomer

(15a)
(15b) α -epoxide

$\Delta^{5,6}$-olefinic ketone match the relevant reference compounds, then the derived $\Delta^{5,10}$-olefinic ketone *must* be identical with or antipodal to either (10b) or (11b). From this the absolute configuration of the furyl olefin at C-8, -9, and -10 can be deduced. To allow an assignment at C-5 one must determine whether the AB ring fusion is *cis* or *trans*. This may be accomplished by preparation of the αβ-unsaturated ketone (8b) by allylic oxidation [2] of the new furyl olefin with chromium trioxide in pyridine. A decision as to the mode of ring fusion may then be made based on the multiplicity of the C-1 methylene

resonance for (8b) when its n.m.r. spectra are recorded for solutions in deuteriochloroform and benzene. With this knowledge the absolute configuration at C-5, -8, -9, and -10 can be assigned. This deals with the final eight possibilities.

The preparation of the two pairs of olefinic ketones (10a and b) and (11a and b), which were required as reference compounds, was undertaken. Epoxidation of the furyl olefin (1), followed by treatment with boron trifluoride and then oxidation, would be expected to give (10a and b). However, not enough of compound (1) was available. Fortunately, the hydroxybutenolides (12a and b), which had been prepared [1] from the naturally occurring epoxybutenolide (13), were relatively abundant. These, upon reduction with di-isobutylaluminium hydride at −20 °C, gave the furyl alcohols (14a and b), which were converted into the desired furyl ketones (10a and b) by oxidation.

The other pair of reference furyl ketones (11a and b) were prepared directly from the known [2] furyl olefin (3a). Epoxidation of (3a) furnished a major (15a) and a minor (15b) epoxide in the ratio *ca.* 3 : 1. The configurations of the epoxide rings in these compounds were not assignable on the basis of n.m.r. evidence [16] because of doubts as to the preferred conformation(s) of the *cis*-decalin systems. However, since treatment of (15a) with boron trifluoride furnished (16a), which has an axial hydroxy-group (see below), the two epoxides can be formulated as shown. Indeed treatment of (15a) with the Lewis acid furnished three products, the major of which was the least polar. The spectral data of this unstable compound agree with its formulation as the aldehyde (17), the result of migration of the 2,3-bond in (15a) to an incipient cationic centre at C-4. The product of intermediate polarity was the $\Delta^{5,6}$-olefinic alcohol (16a). The magnitude of the coupling of H-3 in its n.m.r. spectrum indicates that the hydroxy-group has the axial (β) orientation. The most polar product was the $\Delta^{5,10}$-olefinic alcohol (16b). No trace of the ketone (18) or its C-4 epimer was detected in the products. Oxidation of (16a and b) gave the desired furyl ketones (11a and b). Compound (10a) can be distinguished from (11a) and (10b) from (11b) very readily on the basis of their n.m.r. spectra (see Experimental section). Indeed the n.m.r. spectrum of (10b) is almost identical with that of (19a) [which was prepared from (19b) [1]] except for resonances attributable to the side-chains, and thus (1), (3a), (10a), (10b), (11a), and (11b) may serve as general standards for n.m.r. comparisons with a related compound of unknown stereochemistry irrespective of the composition of its side-chain.

The assignment of stereochemistry in structure (2a) proved uncomplicated. Epoxidation of (2a) was expected to proceed slowly since its high mobility on silver nitrate–silica gel suggests that the olefinic bond is severely hindered. Indeed, upon treatment with *m*-chloroperbenzoic acid more than half the substrate

[16] K. Tori, T. Komeno, and T. Nakagawa, *J. Org. Chem.*, 1964, **29**, 1136.
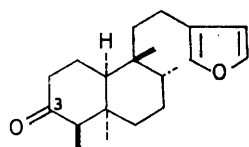
survived even after 24 h, and prolonged reaction led to attack on the furan ring, yielding a complex mixture of
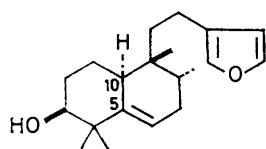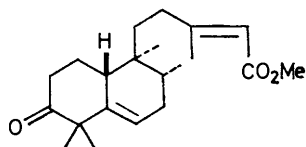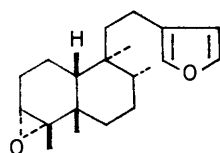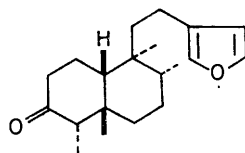

(16a)
(16b) Δ^{5,10}-isomer

(17)

(18)
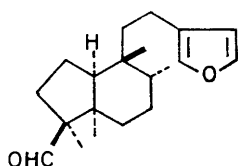
(19a)
(19b) 3β-alcohol

(20)

(21)

polar materials. Thus the yield of the desired product(s) never exceeded 20%. A study of molecular models indicated that the olefinic bond is blocked by bulky groups on both faces, regardless of conformation, but it appeared likely that attack from the β-face might be more favourable. Surprisingly, only one epoxide (20) was formed. Although the H-3 resonance was clearly visible in its n.m.r. spectrum, the configuration at C-3 and -4 could not be assigned from the coupling pattern since the conformation of the decalin system was not known. However, it became clear that the epoxide ring has the α-orientation when treatment of (20) with boron trifluoride produced the alcohol (14a) as the major product. This latter compound was identical with the unsaturated alcohol which had been prepared from the butenolide epoxide (13) *via* (12a). Since (14b) is unaffected by the rearrangement conditions employed it appears likely that in the formation of (14a) epimerisation had not occurred at C-10 and that the furyl olefins (1) and (2a) are identical except in configuration at C-5. Hence the configurations of (2a) at all centres was established by preparing only the unsaturated alcohol (14a) without the additional step of its conversion into the corresponding ketone (10a). No detectable amount of the tetra-substituted olefinic alcohol (14b) was produced from the epoxide (20) with boron trifluoride although substantial

amounts of the ketone (21) and an unstable compound, presumably the aldehyde (22), were present in the product mixture. Reinforcing evidence for the presence of an AB-*cis*-fused system in (2a) was obtained by converting it into the enone (23) by oxidation with chromium trioxide in pyridine. The latter compound exhibits n.m.r. signal patterns characteristic [2] of the C-1 methylene group in a *cis*-fused system of this type. Final confirmation of the stereochemistry of the *cis*-clerodanes from *S. arguta* came [7] from X-ray structural studies of the non-heavy-atom lactone (4).

Certain differences in the composition of the products resulting from boron trifluoride treatment of the two epoxides [(15a) and (20)] with *cis*-fused AB ring systems can be easily explained. Thus the former probably adopts a non-steroid-like [2] conformation, in which case the oxygen substituent is pseudo-equatorial at C-4, whereas in the latter a steroid-like [2] conformation is preferred with the corresponding substituent orientated pseudo-axially. Hydride shift from C-3 to an incipient cationic centre at C-4 would be expected to predominate over migration of the 2,3-bond in (20), whereas the reverse would be expected for (15a). Indeed, the yield of ketone (21) exceeded that of aldehyde (22) from (20) whereas rearrangement of (15a) yielded as the major product the aldehyde (17) and no significant amount of
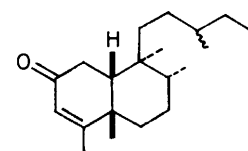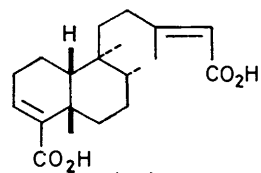

(22)

(23)
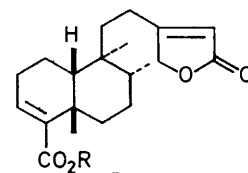

(24)

(25)

(26)
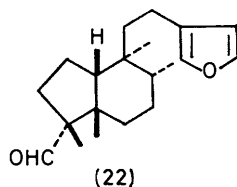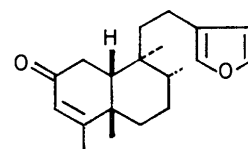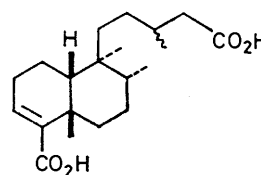
(27)a;β-D-glucopyranosyl
b; Me

the ketone (18). However, the observation that (15a) forms the Δ^{5,6}-olefinic alcohol (16a) and the Δ^{5,10}-olefinic alcohol (16b) whereas (20) apparently forms only the trisubstituted olefin (14a) is less readily rationalised.

Also obscure are the reasons for the pronounced unreactivity of (2a) with *m*-chloroperbenzoic acid and the presence of only one epoxide in the products.

Related cis-*Clerodanes.*—The configuration at C-8 of cistodioic acid (24) has been left [8] unassigned. However, the αβ-unsaturated ketone (23) and the derivative (25) of cistodioic acid have positive Cotton effects for the *n* ⟶ *π** transition of almost identical molecular amplitudes (*a* +65 and +64, respectively), and the related compounds (3b and c),[8,9] with the opposite relative configuration at C-8 have weaker Cotton effects (*a* −46 and −33, respectively). This observation and the fact that the n.m.r. shift patterns for the methyl groups of certain derivatives [8] of cistodioic acid and of related compounds from *S. arguta* are very similar suggests that cistodioic acid may be formulated as (24) with confidence. Haplopappic acid must then be (26), since it has been correlated [10] with cistodioic acid.

The provisional stereochemistry assigned [11] to marrubiaside (27a) has now been confirmed by reducing the related methyl ester (27b) with di-isobutylaluminium hydride to the furyl alcohol (2c). This compound is identical with one of the diterpenoids from *S. arguta*. Linaridial (28) has also been recently [12] correlated with (2a).

A further distinct stereochemical class of cis-clerodanes are those related to columbin [13] (29). Plathyterpol [9] (30) and solidagoic acid A (3d) have been assigned [2] to this group, although evidence for the absolute configuration

(28)

(29)

(30)

(31)

(32) a; 3-furyl
b; butenolide
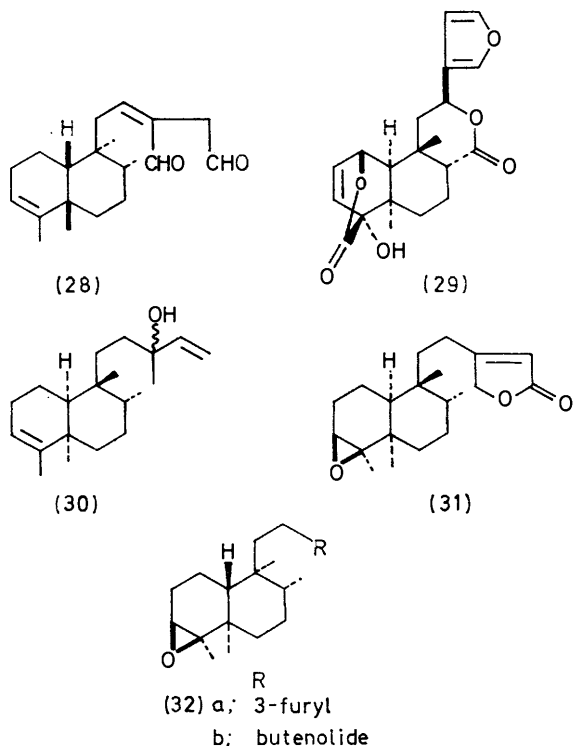
was not entirely conclusive. Optical results from the present study reinforce this conclusion. First, the enones (3b) and (23) have Cotton effects of opposite sign

(*a* −46 and +65, respectively). Secondly, the olefinic ketone (10a) and the related derivative (11a) from solidagoic acid A also have Cotton effects of opposite sign (Δε +1.01 and −0.40, respectively). This provides even more valid evidence for the stereochemical assignment since the fused ring systems of (10a) and (11a) are far less mobile than those of the conjugated enones (3b) and (23). Finally, it appears probable that the clerodanes from [17] *Solidago shortii* belong to this stereochemical class (or the presently unrepresented enantiomeric group). The n.m.r. spectrum of (15a) is strikingly similar to that of the butenolide epoxide (31) from *S. shortii*. Significantly, the shapes of the resonances attributed to the C-3 protons and also the pattern of signals arising from the methyl groups are almost identical. On the other hand, these features differ markedly from those in the n.m.r. spectra of compounds (13), (20), and (32a), and related compounds.[1] Thus, a more likely formulation for the epoxybutenolide from *S. shortii* is (31) rather than that [(32b)] proposed.[17]

EXPERIMENTAL

General details have been outlined previously.[1] Compounds were obtained as oils unless m.p.s are reported. Oils were purified for elemental analysis by distillation *in vacuo* with use of a sublimation block. The coating for silver nitrate-impregnated silica gel chromatoplates contained 10% of silver nitrate. N.m.r. spectra were recorded for solutions in deuteriochloroform unless otherwise indicated. C.d. curves were run for solutions in chloroform with a Cary 61 spectropolarimeter. The o.r.d. data were obtained through the courtesy of Dr. R. A. Haines, Chemistry Department, University of Western Ontario, London, Ontario.

Isolation Procedure.—The ground, air-dried roots and rhizomes (400 g) of *Solidago arguta* Ait. were extracted with ether (Soxhlet) for 8 h. The extract (24 g), which showed several intense spots on analytical t.l.c. after spraying with Ehrlich's reagent, was chromatographed in light petroleum over silica gel (400 g). Fifteen fractions (100 ml) were collected, the first four, eluted with light petroleum and ethyl acetate–light petroleum (1 : 99, 1 : 49, and 1 : 19), being discarded since they were essentially devoid (n.m.r. evidence) of terpenoids. Fractions V (52 mg) and VI (228 mg), eluted with ethyl acetate–light petroleum (1 : 9 and 3 : 17, respectively), were combined and subjected to preparative t.l.c. on silver nitrate–silica gel (light petroleum; run twice). This afforded two minor furan-containing compounds. The more polar of these, the furyl olefin (1) (29 mg), after distillation *in vacuo*, had [α]_D −48° (*c* 1.85) and was identical (n.m.r. and mass spectra, t.l.c. on silver nitrate–silica gel, and g.l.c. retention time [1] of 5.6 min) with the known [1] furyl olefin (1).

The less polar 15,16-*epoxy*-cis-*cleroda*-3,13(16),14-*triene* (2a) (21 mg), after distillation *in vacuo*, had [α]_D +33° (*c* 1.32), ν_max. 873 cm⁻¹; τ (CCl₄) 2.68, 2.79, and 3.76 (all m, 1 H, furanoid), 4.67 (m, H-3, $W_{\frac{1}{2}}$ 7 Hz), 8.28 (d, H₃-18, *J* 1.5 Hz), 8.94 (s, H₃-19), 9.16 (s, H₃-20), and 9.17 (d, H₃-17, *J* 5.5 Hz); g.l.c. retention time 8.2 min (Found: C, 83.8; H, 10.75. $C_{20}H_{30}O$ requires C, 83.85; H, 10.55%).

[17] T. Anthonsen and G. Bergland, *Acta Chem. Scand.*, 1971, **25**, 1924.

Fractions VII (1.20 g), VIII (2.74 g), and IX (1.20 g), eluted with ethyl acetate–light petroleum (1 : 4, 1 : 3, and 3 : 7, respectively), contained the acetate (2b) and an unstable aldehyde (n.m.r. evidence). No attempt was made to identify the latter but the former was isolated by preparative t.l.c. [ethyl acetate–light petroleum (1 : 30), run thrice]. This *acetate* (2b) (1.21 g), after distillation *in vacuo*, had $[\alpha]_D$ $+49°$ (*c* 1.06); $\nu_{max.}$ 1 735 cm^{-1}; τ (CCl$_4$) 2.70, 2.81, and 3.80 (furanoid), 4.33 (m, H-3, $W_{\frac{1}{2}}$ 7 Hz), 5.46br (s, CH$_2$·OAc, $W_{\frac{1}{2}}$ 3 Hz), 8.02 (3 H, s, CO·CH$_3$), 8.80 (s, H$_3$-19), 9.18 (d, H$_3$-17, *J* 5.5 Hz), and 9.20 (s, H$_3$-20) (Found: C, 77.05; H, 9.55. C$_{22}$H$_{32}$O$_3$ requires C, 76.7; H, 9.35%).

Fractions X (3.25 g) and XI (4.55 g), eluted with ethyl acetate–light petroleum (7 : 13 and 2 : 3, respectively), furnished 15,16-*epoxy*-cis-*cleroda*-3,13(16),14-*trien*-19,6α-*olide* (4) (1.8 g) by fractional crystallisation from ether–light petroleum; m.p. (after recrystallisation from the same mixed solvent) 142—143°; $[\alpha]_D$ $+34°$ (*c* 1.07); $\nu_{max.}$ 1 750 cm^{-1}; τ 2.74, 2.87, and 3.84 (furanoid), 3.26 (m, H-3, $W_{\frac{1}{2}}$ 5 Hz; s after irradiation at τ 7.80), 5.78 (dd, H-6; d, *J* 7 Hz after irradiation at τ 8.24 or 8.80), 8.85 (s, H$_3$-19), 9.28 (d, H$_3$-17, *J* 6 Hz), and 9.41 (s, H$_3$-20) (Found: C, 76.6; H, 8.55. C$_{20}$H$_{26}$O$_3$ requires C, 76.4; H, 8.35%).

Preparative t.l.c. [ethyl acetate–light petroleum (1 : 6), run thrice] of the remainder of fractions X and XI afforded, in addition to more of the lactone (4) (1.4 g), the *alcohol* (2c) (2.5 g). After distillation *in vacuo*, the latter had $[\alpha]_D$ $+42°$ (*c* 1.49); $\nu_{max.}$ 3 635 cm^{-1}; τ 2.69, 2.82, and 3.70 (furanoid), 4.38 (m, H-3, $W_{\frac{1}{2}}$ 7 Hz), 5.76br (s, H$_2$-18, $W_{\frac{1}{2}}$ 4 Hz), 8.55br (s, OH, lost on D$_2$O exchange), 8.88 (s, H$_3$-19), 9.20 (d, H$_3$-17, *J* 5.5 Hz), and 9.22 (s, H$_3$-20) (Found: C, 79.05; H, 10.15. C$_{20}$H$_{30}$O$_2$ requires C, 79.4; H, 10.0%).

Fraction XII (1.71 g), eluted with ethyl acetate–light petroleum (7 : 9), furnished by preparative t.l.c. [ethyl acetate–light petroleum (1 : 4), run thrice] the *monoacetate* (2e) (140 mg) and the related *diol* (2d) (165 mg). The *monoacetate* (2e), after distillation *in vacuo*, had $[\alpha]_D$ $+13°$ (*c* 1.40); $\nu_{max.}$ 3 630 and 1 740 cm^{-1}; τ 2.70, 2.83, and 3.76 (furanoid), 4.36 (m, H-3, $W_{\frac{1}{2}}$ 7 Hz), 5.18br (s, H$_2$-18, $W_{\frac{1}{2}}$ 3.5 Hz), 6.55 (m, H-6, $W_{\frac{1}{2}}$ 17 Hz), 7.52br (s, OH, lost on D$_2$O exchange), 7.97 (3 H, s, CO·CH$_3$), 8.72 (s, H$_3$-19), 9.17 (d, H$_3$-17, *J* 6 Hz), and 9.20 (s, H$_3$-20) (Found: C, 73.35; H, 9.15. C$_{22}$H$_{32}$O$_4$ requires C, 73.3; H, 8.95%). The *diol* (2d) had m.p. 103—104° (from light petroleum); $[\alpha]_D$ $+23°$ (*c* 1.58); $\nu_{max.}$ 3 630—3 200 cm^{-1}; τ 2.68, 2.80, and 3.75 (furanoid), 4.40 (m, H-3, $W_{\frac{1}{2}}$ 7 Hz), 5.78br (q, H$_2$-18, J_{AB} 12 Hz, ν_{AB} 6 Hz), 6.44br (s, 2 OH, lost on D$_2$O exchange), 6.60 (m, H-6, $W_{\frac{1}{2}}$ 18 Hz), 8.65 (s, H$_3$-19), 9.15 (d, H$_3$-17, *J* 6 Hz), and 9.20 (s, H$_3$-20) (Found: C, 75.25; H, 9.55. C$_{20}$H$_{30}$O$_3$ requires C, 75.45; H, 9.5%).

Fractions XIII (1.87 g), XIV (2.36 g), and XV (4.07 g), eluted with ethyl acetate–light petroleum (1 : 1), ethyl acetate, and ethyl acetate–acetic acid (99 : 1), respectively, after methylation with diazomethane and preparative t.l.c. [ethyl acetate–light petroleum (1 : 5), run twice] afforded methyl oleanolate (7a) (3.2 g), m.p. 198°, and methyl oleanonate (7b) (1.4 g), m.p. 183—185°. Both were identified by direct comparison with samples prepared from authentic oleanolic acid.

Hydrogenolysis of the Acetate (2b).—A solution of the acetate (940 mg) in ethanol (50 ml) and triethylamine (25 ml) was shaken with hydrogen (5 lb in^{-2}) over palladium-charcoal (5%; 0.8 g) at 20 °C for 2 h. Preparative t.l.c. (light petroleum) of the crude product afforded the furyl olefin (2a) (730 mg), identical {n.m.r. and mass spectra,

$[\alpha]_D$, t.l.c., and g.l.c. retention time (8.2 min)} with the natural product.

Acetylation of the Alcohol (2c).—The alcohol (101 mg) was treated with acetic anhydride–pyridine (1 : 1; 4 ml) at 20 °C for 16 h. Work-up and preparative t.l.c. [ethyl acetate–light petroleum (1 : 15)] afforded the acetate (2b) (98 mg), identical (n.m.r. and i.r. spectra, $[\alpha]_D$, and t.l.c.) with the natural product.

Reduction of the Lactone (4) *with Di-isobutylaluminium Hydride*.—The lactone (351 mg) in anhydrous tetrahydrofuran (10 ml) was reduced under nitrogen with di-isobutyl-aluminium hydride (20% in hexane; 14 ml) at -20 °C for 3.5 h. The product was worked up with acetone (2 ml), diluted with brine, and extracted with ethyl acetate. Preparative t.l.c. [ethyl acetate–light petroleum (2 : 5), run twice] furnished the diol (2d) (269 mg), m.p. 103—104°, identical (n.m.r. and i.r. spectra, $[\alpha]_D$, mixed m.p., and t.l.c.) with the natural product.

Acetylation of the Diol (2d).—Treatment of the diol (265 mg) with acetic anhydride–pyridine (1 : 2; 1.5 ml) at 100 °C for 20 min afforded a mixture of the monoacetate (2e) and the diacetate (2f). The products were separated by preparative t.l.c. [ethyl acetate–light petroleum (1 : 5)]. The monoacetate (140 mg) was identical (n.m.r. and i.r. spectra, $[\alpha]_D$, and t.l.c.) with the natural product. The *diacetate* (108 mg), after distillation *in vacuo*, had $[\alpha]_D$ $+28°$ (*c* 1.20); $\nu_{max.}$ 1 730 cm^{-1}; τ (CCl$_4$) 2.67, 2.82, and 3.78 (furanoid), 4.32 (m, H-3, $W_{\frac{1}{2}}$ 7 Hz), 5.30 (3 H, m, H$_2$-18 + H-6), 8.00 (6 H, s, 2 Ac), 8.85 (s, H$_3$-19), 9.13 (d, H$_3$-17, *J* 6 Hz), and 9.17 (s, H$_3$-20) (Found: C, 71.7; H, 8.85. C$_{24}$H$_{34}$O$_5$ requires C, 71.6; H, 8.5%).

Hydrogenolysis of the Monoacetate (2e).—The diol monoacetate (121 mg) in ethanol (50 ml) and triethylamine (10 ml) was shaken with hydrogen (5 lb in^{-2}) over palladium–charcoal (5%; 110 mg) at 20 °C for 80 min. Preparative t.l.c. [ethyl acetate–light petroleum (1 : 5)] of the product furnished the *mono-ol* (5) which, after distillation *in vacuo*, had $[\alpha]_D$ $+10°$ (*c* 1.00); $\nu_{max.}$ 3 640 cm^{-1}; τ 2.71, 2.83, and 3.80 (furanoid), 4.73 (m, H-3, $W_{\frac{1}{2}}$ 7 Hz), 6.57 (m, H-6, $W_{\frac{1}{2}}$ 17 Hz), 8.15br (s, H$_3$-18), 8.25br (s, OH, lost on D$_2$O exchange), 8.79 (s, H$_3$-19), 9.13 (d, H$_3$-17, *J* 6 Hz), and 9.18 (s, H$_3$-20); τ [with 0.5 mol. equiv. of Eu(dpm)$_3$] 7.10br (s, H$_3$-18), 7.78 (s, H$_3$-19), 8.95 (d, H$_3$-17, *J* 6 Hz), and 8.74 (s, H$_3$-20) (Found: C, 79.4; H, 10.15. C$_{20}$H$_{30}$O$_2$ requires C, 79.4; H, 10.0%).

Hydrogenolysis of the Diacetate (2f).—The diacetate (138 mg) was hydrogenolysed in the manner described above and afforded, after preparative t.l.c. [ethyl acetate–light petroleum (1 : 15)] and distillation *in vacuo*, the *acetate* (2h) (90 mg). This oil had $[\alpha]_D$ $+5°$ (*c* 1.10); $\nu_{max.}$ 1 740 cm^{-1}; τ 2.72, 2.84, and 3.78 (furanoid), 4.72 (m, H-3, $W_{\frac{1}{2}}$ 8 Hz), 5.37 (dd, H-6, *J* 7 and 7 Hz), 7.97 (3 H, s, CO·CH$_3$), 8.15br (s, H$_3$-18), 8.91 (s, H$_3$-19), 9.17 (d, H$_3$-17, *J* 6 Hz), and 9.20 (s, H$_3$-20) (Found: C, 76.9; H, 9.35. C$_{22}$H$_{32}$O$_3$ requires C, 76.7; H, 9.35%).

Reduction of the Acetate (2h).—Reduction of the acetate (87 mg) with an excess of lithium aluminium hydride (1.5 g) in refluxing anhydrous ether (30 ml) for 8 h and work-up afforded an oil. Preparative t.l.c. [ethyl acetate–light petroleum (1 : 5)] gave the mono-ol (2g) (62 mg), identical with the compound prepared from (2e).

Oxidation of the Alcohol (2g).—The alcohol (140 mg) was added in methylene chloride (2 ml) to a stirred solution [4] of chromium trioxide (310 mg) in pyridine (0.5 ml) and methylene chloride (7.5 ml). After 15 min the product

was worked up and the resulting oil subjected to preparative t.l.c. [ethyl acetate–light petroleum (1 : 15)]. This yielded 15,16-*epoxy*-cis-*cleroda*-3,13(16),14-*trien*-6-*one* (6) (77 mg) which, after distillation *in vacuo*, had $[\alpha]_D$ −120° (*c* 1.35); c.d. $[\theta]_{297}$ −15 600°; $\nu_{max.}$ 1 705 cm⁻¹; τ (C₆D₆) 2.82, 2.92, and 3.90 (furanoid), 4.67 (m, H-3, $W_{\frac{1}{2}}$ 7 Hz), 8.48 (d, H₃-18, *J* 1.5 Hz), 8.68 (s, H₃-19), 9.12 (s, H₃-20), and 9.32 (d, H₃-17, *J* 6 Hz); τ 2.69, 2.82, and 3.76 (furanoid), 4.53 (m, H-3, $W_{\frac{1}{2}}$ 7 Hz), 8.48 (d, H₃-18, *J* 1.5 Hz), 8.68 (s, H₃-19), 8.97 (s, H₃-20), and 9.08 (d, H₃-17, *J* 6 Hz) (Found: C, 79.9; H, 9.5. C₂₀H₂₈O₂ requires C, 79.95; H, 9.4%).

Wolff–Kishner Reduction of the Ketone (6).—The ketone (60 mg) was heated with hydrazine (95%; 0.8 ml) at 85 °C for 4 days. Potassium hydroxide (135 mg) was then added and the temperature raised slowly to 205 °C, while the excess hydrazine was allowed to distil out. The mixture was maintained at this temperature for 5.5 h and then allowed to cool. The product was worked up with ethyl acetate–brine and purified by preparative t.l.c. (light petroleum). This afforded the furyl olefin (2a) (6 mg), identical {n.m.r. and i.r. spectra, $[\alpha]_D$, t.l.c., and g.l.c. retention time (8.2 min)} with the natural product.

Oxidation of the Diol (2d).—The diol (69 mg) was oxidised by the Collins' method [4] with chromium trioxide (180 mg) at 20 °C for 1.5 h. The product was worked up with ethanol (1 ml), chloroform (20 ml), and brine. Preparative t.l.c. [ethyl acetate–light petroleum (1 : 8), run twice] afforded the lactone (4) (9.5 mg), m.p. 142—143°, identical (n.m.r. and i.r. spectra, $[\alpha]_D$, t.l.c., and mixed m.p.) with the natural product.

Preparation of the Furyl Ketone (10a).—The butenolide [1] (12a) (102 mg) was treated with di-isobutylaluminium hydride (20% in hexane; 0.5 ml) under nitrogen at −20 °C for 2 h. Work-up and then preparative t.l.c. [ethyl acetate–light petroleum (1 : 10), run thrice] afforded the *furyl alcohol* (14a) (36 mg) which, after distillation *in vacuo*, had $[\alpha]_D$ −36° (*c* 1.71); $\nu_{max.}$ 3 640 cm⁻¹; τ 2.67, 2.78, and 3.74 (furanoid), 4.44 (m, H-6, $W_{\frac{1}{2}}$ 8 Hz), 6.53 (m, H-3, $W_{\frac{1}{2}}$ 7 Hz), 8.86 and 8.94 (both s, H₃-18 and -19), 9.13 (d, H₃-17, *J* 6 Hz), and 9.28 (s, H₃-20); τ (C₆D₆) 2.84, 2.94, and 3.87 (furanoid), 4.50 (m, H-6, $W_{\frac{1}{2}}$ 8 Hz), 6.66 (m, H-3, $W_{\frac{1}{2}}$ 6 Hz), 8.88 and 9.03 (both s, H₃-18 and -19), 9.22 (d, H₃-17, *J* 6 Hz), and 9.33 (s, H₃-20) (Found: C, 79.75; H, 9.85. C₂₀H₃₀O₂ requires C, 79.4; H, 10.0%). This alcohol (14a) (31 mg) was oxidised [4] with chromium trioxide in pyridine–methylene chloride (1 : 2; 4.5 ml) for 15 min. Work-up followed by preparative t.l.c. [ethyl acetate–light petroleum (1 : 10)] furnished the *ketone* (10a) (26 mg), $[\alpha]_D$ −20° (*c* 1.30); c.d. $[\theta]_{291}$ + 3 320°; $\nu_{max.}$ 1 705 cm⁻¹; τ 2.67, 2.78, and 3.73 (furanoid), 4.38 (m, H-6, $W_{\frac{1}{2}}$ 7 Hz), 8.76 (6 H, s, H₃-18 and -19), 9.12 (d, H₃-17, *J* 6 Hz), and 9.31 (s, H₃-20); *m/e* 300 (*M*⁺).

Preparation of the Furyl Ketone (10b).—Reduction of the butenolide (12b) (153 mg) with di-isobutylaluminium hydride as described above and preparative t.l.c. [ethyl acetate–light petroleum (1 : 10), run thrice] of the product afforded the *alcohol* (14b) (36 mg). This, after distillation *in vacuo*, had $\nu_{max.}$ 3 640 cm⁻¹; τ 2.78, 2.91, and 3.91 (furanoid), 6.63 (dd, H-3, $W_{\frac{1}{2}}$ 16 Hz), 8.97 and 9.07 (both s, 3 H, quaternary CMe), 9.13 (d, H₃-17, *J* 6 Hz), and 9.17 (3 H, s, quaternary CMe); τ (C₆D₆) 2.83, 2.90, and 3.87 (furanoid), 6.70 (dd, H-3, $W_{\frac{1}{2}}$ 17 Hz), 8.95 and 9.01 (both s, 3 H, quaternary CMe), 9.17 (d, H₃-17 *J* 6 Hz), and 9.21 (3 H, s, quaternary CMe) (Found: C, 79.65; H, 10.0; C₂₀H₃₀O₂ requires C, 79.4; H, 10.0%). This alcohol (28 mg) was oxidised by the method described above. Preparative

t.l.c. [ethyl acetate–light petroleum (1 : 10)] of the product afforded the *ketone* (10b) (23 mg), $[\alpha]_D$ +77° (*c* 1.17); c.d. $[\theta]_{295}$ + 1 470°; $\nu_{max.}$ 1 710 cm⁻¹; τ 2.69, 2.84, and 3.80 (furanoid), 8.83 and 8.84 (both s, H₃-18 and -19), 9.08 (d, H₃-17, *J* 6 Hz), and 9.10 (s, H₃-20); *m/e* 300 (*M*⁺).

Epoxidation of the Furyl Olefin (3a).—The olefin (3a) (301 mg) was prepared [2] from solidagoic acid A and treated with *m*-chloroperbenzoic acid (300 mg) in carbon tetra-chloride (10 ml) at 20 °C for 2 h. Work-up with ethyl acetate–aqueous sodium carbonate and then preparative t.l.c. [ether–light petroleum (1 : 20), run thrice] furnished two epoxide. The minor, less polar α-*epoxide* (15b) (54 mg) had, after distillation *in vacuo*, $[\alpha]_D$ +12° (*c* 2.20); τ 2.67, 2.83, and 3.75 (furanoid), 7.01 (d, H-3, *J* 2 Hz), 8.76 (s, H₃-18), 8.80 and 9.05 (both s, H₃-19 and -20), and 9.18 (d, H₃-17, *J* 5 Hz) (Found: C, 79.3; H, 10.0. C₂₀H₃₀O₂ requires C, 79.4; H, 10.0%). The major, more polar β-*epoxide* (15a) (164 mg) had, after distillation *in vacuo*, $[\alpha]_D$ −22° (*c* 1.56); τ 2.68, 2.80, and 3.75 (furanoid), 7.01 (d, H-3, *J* 5.5 Hz), 8.70 (s, H₃-18), 8.85 and 9.05 (both s, H₃-19 and -20), and 9.17 (d, H₃-17, *J* 5 Hz) (Found: C, 79.4; H, 10.1%).

Treatment of the Epoxide (15a) *with Boron Trifluoride*.—The major epoxide (130 mg) in anhydrous benzene (5 ml) was treated with boron trifluoride–ether complex (1 ml) at 20 °C for 2 min. Work-up with ethyl acetate–aqueous sodium hydrogen carbonate and preparative t.l.c. [ether–light petroleum (1 : 20), run eleven times] afforded three compounds. The major and least polar product (63 mg) was the *aldehyde* (17) (63 mg) which, after distillation *in vacuo*, had $\nu_{max.}$ 1 710 cm⁻¹; τ 0.30 (s, CHO), 2.68, 2.82, and 3.75 (furanoid), 8.92, 9.05, and 9.12 (all s, 3 H, quaternary CMe), and 9.17 (d, H₃-17, *J* 5 Hz) (Found: C, 79.25; H, 9.75. C₂₀H₃₀O₂ requires C, 79.4; H, 10.0%).

The product (29 mg) of intermediate polarity was the Δ⁵,⁶-*olefinic alcohol* (16a) which, after distillation *in vacuo*, had $[\alpha]_D$ −45° (*c* 1.43); τ 2.67, 2.81, and 3.75 (furanoid), 4.53 (m, H-6, $W_{\frac{1}{2}}$ 8 Hz), 6.55 (m, H-3, $W_{\frac{1}{2}}$ 6 Hz), 8.92 (6 H, s, two quaternary CMe), 9.09 (3 H, s, quaternary CMe), and 9.18 (d, H₃-17, *J* 6 Hz) (Found: C, 79.2; H, 10.1. C₂₀H₃₀O₂ requires C, 79.4; H, 10.0%).

The most polar product (24 mg) was the Δ⁵,¹⁰-*olefinic alcohol* which, after distillation *in vacuo*, had $[\alpha]_D$ +25° (*c* 1.20); τ 2.67, 2.82, and 3.75 (furanoid), 6.48 (dd, H-3, $W_{\frac{1}{2}}$ 14 Hz), 8.94 (3 H, s, quaternary CMe), 8.97 (6 H, s, two quaternary CMe), and 9.04 (d, H₃-17, *J* 6 Hz) (Found: C, 79.8; H, 10.3%).

Preparation of the Ketones (11a *and* b).—The alcohol (16a) (23 mg) upon oxidation by the Collins' method [4] afforded the *ketone* (11a) (19 mg), which was purified by preparative t.l.c. [ethyl acetate–light petroleum (1 : 10)]. It had $[\alpha]_D$ −120° (*c* 1.77); c.d. $[\theta]_{305}$ −1 300°; τ 2.62, 2.74, and 3.70 (furanoid), 4.43 (m, H-6, $W_{\frac{1}{2}}$ 8 Hz), 8.76, 8.78, and 9.07 (all s, 3 H, quaternary CMe), and 9.10 (d, H₃-17, *J* 6 Hz); *m/e* 300 (*M*⁺).

The alcohol (16b) (20 mg) was oxidised by the Collins' method.[4] Preparative t.l.c. [ethyl acetate–light petroleum (1 : 10)] furnished the *ketone* (11b) (17 mg), $[\alpha]_D$ −2.5° (*c* 1.57); c.d. $[\theta]_{300}$ −271°; τ 2.66, 2.79, and 3.74 (furanoid), 8.83 (6 H, s, two quaternary CMe), 8.92 (3 H, s, quaternary CMe), and 8.99 (d, H₃-17, *J* 6 Hz); *m/e* 300 (*M*⁺).

Preparation of the Oxo-ester (19a).—The alcohol (47 mg), prepared [1] from methyl kolavenate, was oxidised by Collins' method [4] at 20 °C for 15 min. Preparative t.l.c. [ethyl acetate–light petroleum (1 : 5), run twice] furnished the

oxo-ester (19a) (42 mg), $[\alpha]_D$ $+32°$ (c 1.44); $\nu_{max.}$ 1 705 and 1 670 cm^{-1}; τ 4.34 (m, H-14, $W_{\frac{1}{2}}$ 4 Hz), 6.32 (3 H, s, OCH$_3$), 7.83 (d, H$_3$-16, J 1 Hz), 8.82, 8.84, and 9.10 (all s, 3 H, quaternary CMe), and 9.10 (d, H$_3$-17, J 6 Hz); m/e 332 (M^+).

Epoxidation of the Furyl Olefin (2a).—The olefin (710 mg) was treated with *m*-chloroperbenzoic acid (85%; 650 mg) in carbon tetrachloride (10 ml) at 20 °C for 3 h. Work-up with ethyl acetate–aqueous sodium carbonate and preparative t.l.c. [ethyl acetate–light petroleum (1 : 30) run twice] furnished the epoxide (20) (141 mg) and the substrate (127 mg). No attempt was made to identify the components of a mixture of more polar products. The *epoxide* (20), after distillation *in vacuo*, had $[\alpha]_D$ $+4°$ (c 1.36); τ (CCl$_4$) 2.72, 2.85, and 3.82 (furanoid), 7.23 (m, H-3, $W_{\frac{1}{2}}$ 5 Hz), 8.73 (s, H$_3$-18), 8.93 (s, H$_3$-19), 9.13 (s, H$_3$-20), and 9.14 (d, H$_3$-17, J 6 Hz) (Found: C, 79.25; H, 10.1. C$_{20}$H$_{30}$O$_2$ requires C, 79.4; H, 10.0%).

Treatment of the Epoxide (20) *with Boron Trifluoride.*—Treatment of the epoxide (136 mg) in anhydrous carbon tetrachloride (5 ml) with boron trifluoride–ether complex (1 ml) at 20 °C for 5 min and work-up with ethyl acetate–water gave an oil (115 mg). Preparative t.l.c. [ethyl acetate–light petroleum (1 : 10), run thrice] afforded two products. The more polar (51 mg) had $[\alpha]_D$ $-33°$ (c 1.27) and was identical [n.m.r. (in CDCl$_3$ and C$_6$D$_6$), i.r., and mass spectra, and t.l.c.] with the alcohol (14a) prepared from the butenolide epoxide (13). The less polar product was the *ketone* (21) (22 mg) which, after distillation *in vacuo*, had c.d. $[\theta]_{288}$ -4 280°; τ (CCl$_4$) 2.78, 2.85, and 3.80 (furanoid), 8.85 (s, H$_3$-19), 9.10 (6 H, d, H$_3$-17 and -18, both J 6 Hz), and 9.17 (s, H$_3$-20); τ (C$_6$H$_6$) 8.98 (d, H$_3$-18, J 6 Hz), 9.25 (s, H$_3$-19), 9.27 (s, H$_3$-20), and 9.29 (d, H$_3$-17, J 6 Hz) (Found: C, 79.15; H, 9.83. C$_{20}$H$_{30}$O$_2$ requires C, 79.4; H, 10.0%).

Allylic Oxidation of the Furyl Olefin (2a).—The olefin

(150 mg) in pyridine (5 ml) was treated [2] with chromium trioxide at 20 °C in the dark for 12 days. Preparative t.l.c. [ethyl acetate–light petroleum (1 : 8), run thrice] afforded the *enone* (23) (62 mg), which, after distillation *in vacuo*, had $[\alpha]_D$ $+26°$ (c 0.92); c.d. $[\theta]_{334}$ $+5$ 100°; o.r.d. a $+65°$ (ethanol; λ 332 nm); $\lambda_{max.}$ 245 nm; $\nu_{max.}$ 1 668 cm^{-1}; τ (CCl$_4$) 2.65, 2.77, and 3.73 (furanoid), 4.18 (m, H-3, $W_{\frac{1}{2}}$ 3 Hz), 7.35 (m, H$_2$-1, $W_{\frac{1}{2}}$ 7 Hz), 8.00 (d, H$_3$-18, J 1.5 Hz), 8.68 (s, H$_3$-19), 9.08 (d, H$_3$-17, J 6 Hz), and 9.32 (s, H$_3$-20); τ (C$_6$H$_6$) 7.40 (d, H$_2$-1, J_{obs} 4 Hz), 8.48 (d, H$_3$-18, J 1.5 Hz), 9.08 (s, H$_3$-19), 9.35 (d, H$_3$-17, J 6 Hz), and 9.44 (s, H$_3$-20) (Found: C, 79.9; H, 9.6. C$_{20}$H$_{28}$O$_2$ requires C, 79.95; H, 9.4%).

Reduction of the Marrubiaside Derivative (27b).—The methyl ester (27b) (104 mg) in anhydrous tetrahydrofuran (5 ml) was treated under nitrogen with di-isobutylaluminium hydride (20% in hexane; 10 ml) at -20 °C for 2 h. Acetone (1 ml) and then brine (10 ml) were added. This mixture was extracted with ethyl acetate and the extract was washed successively with dilute aqueous sulphuric acid, aqueous sodium hydrogen carbonate, and brine. The product was subjected to preparative t.l.c. [ethyl acetate–light petroleum (1 : 5), run twice] and afforded, in addition to the substrate (22 mg), the alcohol (2c) (20 mg), $[\alpha]_D$ $+36°$ (c 1.77), identical (n.m.r. and i.r. spectra and t.l.c.) with the constituent of *S. arguta*.