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AN INVESTIGATION OF THE USE OF L-ASCORBIC ACID AND ITS DERIVATIVES IN THE SYNTHESIS OF SPIRODILACTONES*†

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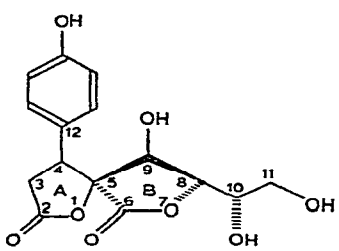
ABSTRACT

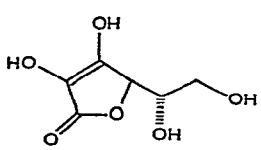
Treatment of alkyl 3-bromo-3-phenylpropionates (**8**) with the ambident L-ascorbate anion (**9**) did not yield *C*- or *O*-substituted derivatives of L-ascorbic acid. Instead, the corresponding (*E*)-cinnamates **11** or 3-hydroxypropionic acid (**12**) were obtained, depending on whether alkaline or acidic conditions were used. Successive unimolar methylation and (*E*)-cinnamoylation of 5,6-*O*-isopropylidene-L-ascorbic acid (**14**) furnished 2-*O*-(*E*)-cinnamoyl-5,6-*O*-isopropylidene-3-*O*-methyl-L-ascorbic acid (**17**), which was transformed into the isomeric 2-*C*-methyl derivative **18** on attempted demethylation with lithium iodide in *N*,*N*-dimethylformamide.

INTRODUCTION

Leucodrin[2] (**1**) and conocarpin[3] (**2**) are members of a group of naturally occurring spirodilactones having the 1,7-dioxa-2,6-dioxospiro[4.4]nonane skeleton in common, and for which part of the skeleton resembles L-ascorbic acid (**3**) in a reduced form. Leucodrin (**1**) is the major constituent of the leaves of *Leucadendron* species[2], while conocarpin has been isolated[3] from the dried leaves of *Leucospermum*



1 leucodrin (4*R*,5*S*,8*R*,9*R*,10*S*)
2 conocarpin (4*S*,5*S*,8*R*,9*R*,10*S*)



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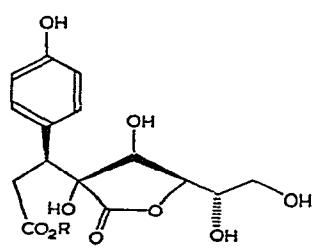
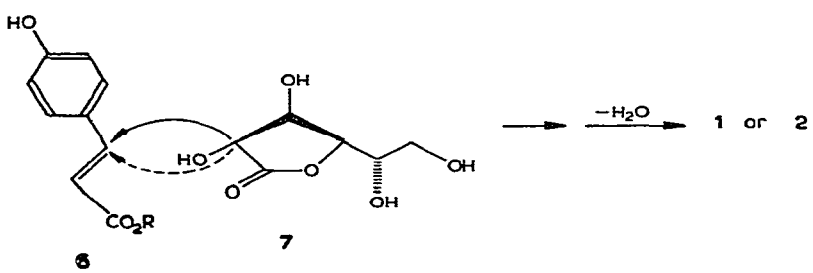


4 R = H
5 R = Me

*Dedicated to the memory of Dr. Hewitt G. Fletcher, Jr.
†Synthetic Studies on Spirodilactones: Part II[1].

reflexum, from which two closely related, ring-A-opened lactones, conocarpic acid (**4**) and reflexin (**5**), were also obtained[4]. Reflexin (**5**) is transformed into conocarpin (**2**) by alkaline hydrolysis and relactonization. Chemical[5–8], spectroscopic[3,8], and X-ray diffraction[9] investigations spanning many years have firmly established the structural relationships[3,4] between leucodrin (**1**), conocarpin (**2**), conocarpic acid (**4**), and reflexin (**5**).

In view of the stereochemical relationship between leucodrin (**1**) and conocarpin (**2**), it has been suggested[9] that their synthesis in plants might involve a Michael condensation of *p*-hydroxy-(*E*)- or -(*Z*)-cinnamic acid (*e.g.*, **6**, R = H) and L-galactono-1,4-lactone (**7**) (or a related structure), followed by lactonization of the adduct. Thus, the direction from which this addition occurs would determine whether leucodrin (**1**) or conocarpin (**2**) was formed subsequently. Although the postulated occurrence of L-galactono-1,4-lactone in higher plants is somewhat speculative, enzymic oxidation of galactitol or a sequence of enzymic oxidation and reduction of D-galactose could conceivably provide a route to this lactone[4]. Indeed, Isherwood *et al.*[10] and others[11] have shown that the lactones of D-galacturonic acid and L-galactonic acid are converted into L-ascorbic acid by enzymes present in rat liver and in cress seedlings. Alternatively, an intramolecular Michael addition of the esterified (with L-galactono-1,4-lactone) *p*-coumaric acid might furnish the spirodilactone system. The isolation of D-fructosyl *p*-coumarate (pajaneelin) from *Pajaneelia rheedii*[12] and of D-glucosyl *p*-coumarate from the petals and leaves of a variety of plants (*e.g.*, *Petunia hybria*)[13] has established the occurrence of glycosyl *p*-coumarates in Nature.

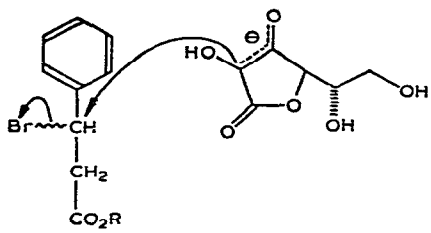


6 **7**

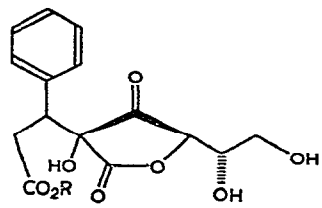
DISCUSSION

The speculative biosynthetic routes to leucodrin (**1**) and conocarpin (**2**) are of more than passing interest, since they point the way to possible chemical syntheses of these compounds. In particular, the realization that the B-rings of leucodrin and conocarpin bear a resemblance to L-ascorbic acid (**3**) led us to investigate the reaction between alkyl 3-bromo-3-phenylpropionates (**8**) and the L-ascorbate anion (**9**), since 2-*C*-alkylation would yield a product **10** related to reflexin (**5**), albeit with a carbonyl group instead of an hydroxyl group attached to the lactone ring. In general, *C*-alkylation of L-ascorbic acid should be favoured in polar, protic solvents (*e.g.*,

water)[14], whereas *O*-alkylation should predominate in aprotic solvents (*e.g.*, *N,N*-dimethylformamide)[15]. However, treatment of potassium L-ascorbate with either methyl or butyl 3-bromo-3-phenylpropionate (**8**, R = Me or Bu) in aqueous acetone gave the corresponding (*E*)-cinnamates (**11**, R = Me or Bu) as the products of dehydrohalogenation; the tendency for *β*-halogeno acids to eliminate hydrogen halide under basic conditions is well-established[16]. Products arising from a direct displacement on **8** or from Michael addition to the resulting cinnamates **11** (R = Me or Bu) were not observed; L-ascorbic acid also failed to condense with ethyl cinnamate (**11**, R = Et) in *N,N*-dimethylformamide under basic conditions. An attempt to effect the 2-*C*-alkylation of **9** with the methyl ester **8** (R = Me) under acidic conditions led to solvolysis and de-esterification, with the formation of 3-hydroxy-3-phenylpropionic acid (**12**). The products obtained in the foregoing reactions were identified by comparison with authentic samples or by analytical and spectroscopic data.



8 **9**



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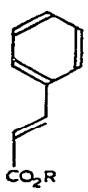

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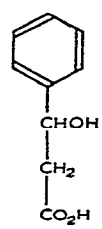

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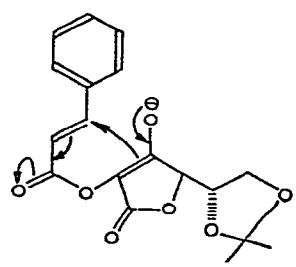

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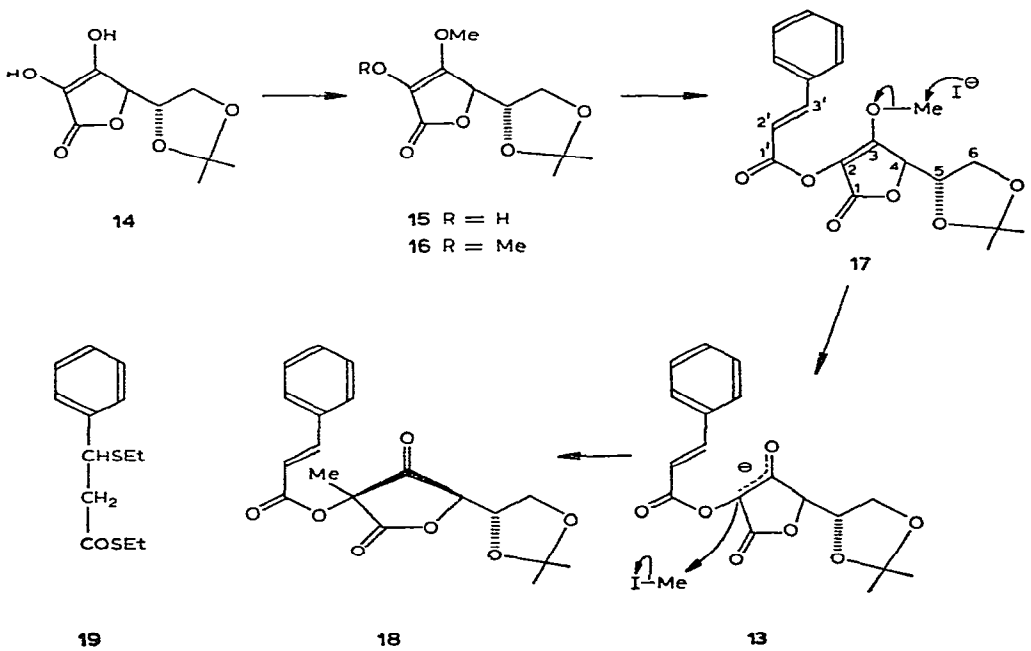
Since attempts to obtain progenitors of the spirodilactone skeleton by intermolecular reaction of the L-ascorbate anion (**9**) were unsuccessful, we hoped that intramolecular cyclization of the enolate anion (**13**) derived from 2-*O*-(*E*)-cinnamoyl-5,6-*O*-isopropylidene-L-ascorbic acid might be more readily achieved. Since cinnamoylation of O-2 cannot be accomplished directly, this approach requires the protection of O-3 of an L-ascorbic acid derivative by a group that can be removed after cinnamoylation without disruption of the ester and olefinic linkages. Since dealkylation of enol ethers can be accomplished by a variety of methods[17] suitable for our purpose, we undertook a synthesis of 2-*O*-(*E*)-cinnamoyl-5,6-*O*-isopropylidene-

3-*O*-methyl-L-ascorbic acid (**17**) and examined its dealkylation with nucleophilic reagents.

Acetonation of L-ascorbic acid afforded the known[18] 5,6-*O*-isopropylidene derivative **14**, which reacted with diazomethane in ether to give a separable mixture of the 3-methyl ether **15** and the 2,3-dimethyl ether **16**. Both **15** and 3-*O*-methyl-L-ascorbic acid were non-reducing towards iodine in acid solution, gave an intense violet–blue colour with a solution of ferric chloride, and displayed a strong absorption band at 247 nm, which was shifted to 268–270 nm following the addition of alkali[19]. This evidence is compatible with the structure assigned to the monomethylated derivative **15**. Although a previous attempt to acetylate HO-2 in L-ascorbic acid by the usual methods had failed[20], 2-*O*-(*E*)-cinnamoyl-5,6-*O*-isopropylidene-3-*O*-methyl-L-ascorbic acid (**17**) was readily obtained from **15** on treatment with (*E*)-cinnamoyl chloride in *N*,*N*-dimethylformamide in the presence of sodium hydride. Analytical and spectroscopic data (see Experimental) supported the structure assigned.



14 15 R = H 16 R = Me 17 19 18 13

It seemed that demethylation of **17**, to furnish the enolate anion **13**, would best be accomplished by an S_N2 reaction. Treatment of **17** with lithium iodide[21] in methyl sulphoxide (or in *N*,*N*-dimethylformamide) at ~80° produced a dark-red solution from which a crystalline compound ($C_{19}H_{20}O_7$) isomeric with **17** was isolated in low yield (~36%) by chromatography. The infrared spectra of this product and **17** differed significantly; in addition to absorptions appearing at 1630 (C=C) and

1725 cm^{-1} (α,β-unsaturated ester), the former exhibited bands at 1805 and 1760 cm^{-1} that were attributed to the presence of a saturated γ-lactone and a five-membered β-ketolactone[22], respectively. The ^{1}H-n.m.r. spectrum also furnished useful structural information; in particular, a three-proton singlet at τ 8.26 was assigned (by its chemical shift and lack of multiplicity) to a methyl group attached to a tertiary carbon atom, possibly flanked on either side by a carbonyl group and/or deshielded by the aromatic ring. The accumulated evidence suggested that **17** reacted with lithium iodide in dipolar, aprotic solvents to give 2-*O*-(*E*)-cinnamoyl-5,6-*O*-isopropylidene-2-*C*-methylhex-3-ulosono-1,4-lactone (**18**), although the spectroscopic data did not permit the stereochemistry at C-2 to be assigned.

The transformation of **17** into **18** may have been induced thermally, since related thermal rearrangements of $\alpha\beta$-unsaturated ethers are known; for example, ethoxystyrene ($PhCH{=}CHOC_2H_5$) rearranges to butyrophenone ($PhCOC_3H_7$) on heating[23]. However, such rearrangements are not general[24], and **17** could not be induced to undergo a rearrangement on prolonged heating in methyl sulphoxide. A more likely explanation is that the enolate anion **13**, arising from demethylation of **17**, is remethylated at C-2 by the liberated methyl iodide. Attempts to remove methyl iodide from the reaction medium before it reacted were unsuccessful.

Demethylation of **17** was then attempted using thioethoxide anions[25], since ethyl methyl sulphide resulting from a successful reaction should show no tendency to alkylate the enolate anion **13**. However, the reaction of **17** with thioethoxide anions in *N*,*N*-dimethylformamide furnished 5,6-*O*-isopropylidene-3-*O*-methyl-L-ascorbic acid (**15**) (identified by comparison with an authentic sample) and a pungent, sulphur-containing liquid identified as *S*-ethyl 3-ethylthio-3-phenyl(thiopropionate) (**19**). A detailed analysis of the ^{1}H-n.m.r. spectrum of the thioester **19** is given in the Experimental section, and it suffices to note that the spectrum revealed the presence of a phenyl group, a methine proton (triplet), methylene protons (doublet), and two ethylthio groups in different environments, and the absence of olefinic protons. The formation of **19** is readily rationalized by nucleophilic attack of thioethoxide anions at both the olefinic linkage and the ester carbonyl group of **17**, with the expulsion of **15** as the anion.

Although the demethylation of 2-*O*-(*E*)-cinnamoyl-5,6-*O*-isopropylidene-3-*O*-methyl-L-ascorbic acid (**17**) can be assumed to occur with lithium iodide, the inability of the enolate anion **13** to cyclize with the activated double-bond is disconcerting from a synthetic viewpoint. Inspection of a Dreiding model of **17** showed that the internuclear distance between C-2 and C-3′ is ~3 Å, which would account for the preference of the enolate anion **13** to react with an external reagent. If this explanation is correct, future efforts to synthesise spirodilactones of this type must inevitably focus on the cyclization of systems in which this carbon–carbon bond is already formed. The synthesis of systems related to conocarpic acid (**4**) are currently underway in our laboratory, since such systems are known[4] to give spirodilactones on lactonization.

EXPERIMENTAL

Thin-layer chromatography (t.l.c.) was performed on Kieselgel G; the chromatograms were first examined under ultraviolet light, after which the components were detected with vanillin–sulphuric acid[26]. Preparative chromatography was carried out on silica gel MFC (Hopkin and Williams). Infrared (i.r.) spectra were generally recorded for Nujol mulls on a Perkin–Elmer Infracord spectrometer, and ultraviolet spectra were recorded on a Unicam SP 800 spectrophotometer. ^{1}H-N.m.r. spectra were obtained with a Perkin–Elmer R10 spectrometer (60 MHz) for solutions in $CDCl_3$ (internal Me_4Si). Precise mass measurements were obtained at the Physicochemical Measurements Unit, Harwell, Bucks.

Butyl 3-bromo-3-phenylpropionate (**8**, *R* = *Bu*). — A solution of 3-bromo-3-phenylpropionic acid[27] (10 g) in 1-butanol (50 ml) at 0° was saturated with hydrogen bromide, and, after being kept at room temperature for 72 h, the solution was filtered and the filtrate was dispersed in cold water. The yellow oil that separated was extracted with light petroleum (b.p. 40–60°, 3 × 50 ml), and the combined extracts were dried ($CaCl_2$ and $CaCO_3$) and evaporated. Distillation of the residue gave the butyl ester **8** (R = Bu) (9 g), b.p. 120°/12 mmHg, ν_{max} (film) 1725 cm^{-1} (ester) (Found: C, 54.5; H, 5.8; Br, 27.7. $C_{13}H_{17}BrO_2$ calc.: C, 54.7; H, 6.0; Br, 28.1%). N.m.r. data: τ 2.91 (5 aromatic protons), 4.41 (t, 1 H, C*H*BrCH$_2$), 5.77 (t, 2 H, $CO_2CH_2CH_2$), 6.60 (d, 2 H, CHBrCH_2CO), 8.18–8.84 (m, 4 H, $CH_2CH_2CH_2CH_3$), and 9.06 (t, 3 H, CH_2CH_3).

Methyl 3-bromo-3-phenylpropionate (**8**, R = Me) (89%), m.p. 37–38° [from light petroleum (b.p. 60–80°)], was similarly prepared from 3-bromo-3-phenylpropionic acid and methanol; lit.[28] m.p. 37.5–38.5°.

Attempted condensation of methyl 3-bromo-3-phenylpropionate (**8**, *R* = *Me*) *with* L-*ascorbic acid* (**3**). — (*a*) *In the presence of a base.* A solution of L-ascorbic acid (1.46 g) in water (20 ml) was partly neutralized with a solution of potassium hydroxide (0.43 g) in water (5 ml), whereafter it was stirred with a solution of the methyl ester of **8** (2.1 g) in acetone (40 ml) for 72 h at room temperature. The organic solvent was then evaporated and the aqueous solution was extracted with light petroleum (b.p. 40–60°, 4 × 30 ml); the combined extracts were dried ($MgSO_4$) and evaporated to yield methyl (*E*)-cinnamate (**11**, R = Me) (1.01 g, 72%), b.p. 139–142°/12 mmHg, which was identified by comparison with an authentic sample; lit.[29] b.p. 142–145°/20 mmHg.

The reaction of L-ascorbic acid (2.2 g) with butyl 3-bromo-3-phenylpropionate (**8**, R = Bu) (3.5 g) under comparable conditions furnished butyl (*E*)-cinnamate (**11**, R = Bu) (2.1 g), b.p. 104°/0.7 mmHg, ν_{max} (film) 1720 and 1660 cm^{-1} (C=C–C=O) (Found: C, 76.4; H, 7.8. $C_{13}H_{16}O_2$ calc.: C, 76.5; H, 7.8%). N.m.r. data: τ 2.68 (5 aromatic protons), 2.94 (dd, 2 H, ν_{AB} 75.5 Hz, J_{AB} 16.6 Hz, *trans*-C*H*=C*H*), 5.81 (t, 2 H, $CO_2CH_2CH_2$), 8.18–8.84 (m, 4 H, $CH_2CH_2CH_2CH_3$), and 9.06 (t, 3 H, CH_2CH_3).

(*b*) *In acid solution.* — A buffered solution (15 ml) of L-ascorbic acid (2.2 g) at

pH 4 (B.D.H. buffer powder) was stirred with a solution of the methyl ester **8** (R = Me) (3 g) in acetone (15 ml) for one week at room temperature. The organic solvent was then evaporated and the aqueous solution was extracted with light petroleum (b.p. 60–80°, 50 ml). The aqueous layer was exhaustively extracted with ethyl acetate, and the extract was dried ($MgSO_4$) and concentrated. Chromatography of the residue on silica gel (elution with chloroform containing 1% of acetic acid) gave 3-hydroxy-3-phenylpropionic acid (**12**; 1.7 g, 82%), m.p. 94–95° (from toluene), ν_{max} 3500 (OH) and 1700 cm^{-1} (CO_2H); lit.[30] m.p. 96°.

*5,6-O-Isopropylidene-*L*-ascorbic acid* (**14**). — A solution of L-ascorbic acid (10 g) in acetone (500 ml), in which was suspended anhydrous copper(II) sulphate (500 g), was stirred for 24 h at room temperature, after which time solids were filtered off and the filtrate was concentrated. Trituration of the resulting syrup with light petroleum (b.p. 40–60°) deposited needles of the acetal **14** (9.3 g, 75%), m.p. 217–219° (dec.), $[\alpha]_D$ +11.5° (*c* 1, chloroform); lit.[18] m.p. 220–222° (dec.), $[\alpha]_D$ +15° (*c* 1, ethanol).

*3-O-Methyl-5,6-O-isopropylidene-*L*-ascorbic acid* (**15**). — To a solution of the acetalated acid **14** (4 g) in dry methanol (10 ml) at −10° was gradually added an ethereal solution of diazomethane (~4.6 mol.), whereafter removal of the solvents left a pale-yellow syrup. Chromatography on silica gel [elution with acetone–light petroleum (b.p. 60–80°), 1:4] gave first 5,6-*O*-isopropylidene-2,3-di-*O*-methyl-L-ascorbic acid (**16**) (in yields ranging from 10% to 20%), m.p. 98.5–99.5° [from light petroleum (b.p. 80–100°)], $[\alpha]_D$ +11° (*c* 1, chloroform), ν_{max} 1745 ($\alpha\beta$-unsaturated lactone) and 1670 cm^{-1} (C=C) (Found: C, 54.4; H, 6.7. $C_{11}H_{16}O_6$ calc.: C, 54.1; H, 6.6%). N.m.r. data: τ 5.36–5.49 (m, 1 H), 5.64–5.92 (m, 3 H), 5.75 and 6.07 (2 s, 6 H, 2 MeO), and 8.62 (s, 6 H, CMe_2). Continued elution gave the methyl ether **15** (2.14 g, 50%), m.p. 116–117° [from toluene–light petroleum (b.p. 80–100°)], $[\alpha]_D$ +11° (*c* 1, chloroform); λ_{max} (ethanol): 247 nm (shifted to 268–270 nm on the addition of dilute sodium hydroxide solution); ν_{max} 3320 (OH), 1750 and 1685 cm^{-1} (typical pattern for ascorbate derivatives)[31] (Found: C, 51.8; H, 5.8. $C_{10}H_{14}O_6$ calc.: C, 52.2; H, 6.1%). N.m.r. data: τ 3.63 (broad s, 1 H, OH, exchangeable with D_2O), 5.38–5.83 (2 m, 4 H), 5.75 (s, 3 H, OMe), and 8.59 (s, 6 H, CMe_2). The prismatic crystals tended to revert to an amorphous form on storage.

When methylation of the acetal **14** (8 g) in *p*-dioxane (100 ml) was effected with an ethereal solution of diazomethane (~1.5 mol.), the di- and mono-methyl ethers, **16** and **15**, were obtained in yields of 9% and 59%, respectively.

*2-O-(E)-Cinnamoyl-5,6-O-isopropylidene-3-O-methyl-*L*-ascorbic acid* (**17**). — A solution of **15** (1.9 g) in dry *N,N*-dimethylformamide (25 ml) containing sodium hydride (0.2 g) was stirred until the evolution of hydrogen had ceased, whereupon (*E*)-cinnamoyl chloride (1.4 g) was added and stirring was continued for 2 h at room temperature. After the mixture had been dispersed in ice–water, the aqueous solution was extracted with ether (3 × 50 ml), and the ethereal extracts were washed with a solution of sodium hydrogen carbonate (20 ml) and water (30 ml), and dried ($MgSO_4$). Removal of the solvent left a thick syrup (1.8 g, 62%), which on chromatography on

silica gel [elution with acetone–light petroleum (b.p. 60–80°), 1:4] gave the cinnamate **17**, m.p. 121–122° [from benzene–light petroleum (b.p. 60–80°)], $[\alpha]_D$ +30° (*c* 1, chloroform); λ_{max} (ethanol): 285 (ε 1.52×10^5) and 225 nm (ε 1.39×10^5); ν_{max} 1770 (lactone), 1725 and 1670 (C=C–C=O), and 1630 cm^{-1} (C=C) (Found: C, 63.7; H, 5.6. M^+ 360.1195. $C_{19}H_{20}O_7$ calc.: C, 63.3; H, 5.5%. M^+ 360.1209). N.m.r. data: τ 2.80 (s, 5 aromatic protons), 3.05 (dd, 2 H, ν_{AB} 83.5 Hz, J_{AB} 17 Hz, *trans*-C*H*=C*H*), 5.63 (d, 1 H, *J* 2.6 Hz, H-4), 5.67–6.06 (m, 3 H), 6.22 (s, 3 H, OMe), and 8.66 and 8.72 (2 s, 6 H, CMe_2).

Attempted demethylation and cyclization of 2-O-(E)-*cinnamoyl-5,6-*O-*isopropylidene-3-*O-*methyl-*L-*ascorbic acid* (**17**). — (*a*) *With lithium iodide.* The following procedure is typical. A solution of the cinnamate **17** (0.3 g) in *N,N*-dimethylformamide (25 ml) containing lithium iodide monohydrate (0.13 g) was heated at 80° for 30 h, the mixture was then poured into water, and the aqueous solution was extracted with ether (3 × 30 ml). The ethereal extracts were dried ($MgSO_4$) and evaporated, and the residue was chromatographed on silica gel [elution with chloroform–light petroleum (b.p. 80–100°), 1:4] to give first 2-*O*-(*E*)-cinnamoyl-5,6-*O*-isopropylidene-2-*C*-methylhex-3-ulosono-1,4-lactone (**18**) (80 mg, 36%), m.p. 131–132° [from light petroleum (b.p. 80–100°)], $[\alpha]_D$ +156° (*c* 0.3, chloroform); λ_{max} (ethanol): 283 (ε 3.26×10^4), 226 (ε 1.65×10^4), and 220 nm (ε 1.65×10^4); ν_{max} 1805 and 1760 (β-ketolactone), 1725 ($\alpha\beta$-unsaturated C=O) and 1630 cm^{-1} (C=C) (Found: M^+ 360.1221. $C_{19}H_{20}O_7$ calc.: M^+ 360.1209). N.m.r. data: τ 2.51 (s, 5 aromatic protons), 2.85 (dd, 2 H, ν_{AB} 80.6 Hz, J_{AB} 16.7 Hz, *trans*-C*H*=C*H*), 4.98 (broad s, 1 H, H-4), 4.99–5.80 (m, 3 H), 8.26 (s, 3 H, CMe), and 8.66 and 8.72 (2 s, 6 H, CMe_2). Continued elution gave only starting material and a small proportion of an unidentified syrup.

An analogous mixture of components was obtained when demethylation was attempted with lithium iodide in either methyl sulphoxide or 2,4,6-collidine.

(*b*) *With thioethoxide in* N,N-*dimethylformamide.* — To a solution of ethanethiol (5 ml) in *N,N*-dimethylformamide (20 ml) was carefully added sodium hydride (20 mg), and, when effervescence had ceased, the mixture was heated at 80° for a few minutes to remove the excess of the thiol. The cinnamate **17** (0.31 g) was then added and the temperature was maintained at 80° for 6 h, when t.l.c. showed that no starting material remained. The solvent was removed, and the residue was dispersed in aqueous acetic acid which was then extracted with ether (3 × 40 ml). The ethereal extracts were washed with water (15 ml), dried ($MgSO_4$), and concentrated. Chromatography of the residue on silica gel [elution with ether–light petroleum (b.p. 80–100°), 1:1] furnished *S*-ethyl 3-ethylthio-3-phenyl(thiopropionate) (**19**; 0.19 g, 86%), b.p. 96°/8 mmHg, ν_{max} (film) 1675 cm^{-1} (C=O) (Found: C, 61.6; H, 6.8; S, 25.5. $C_{13}H_{18}OS_2$ calc.: C, 61.4; H, 7.1; S, 25.2%). N.m.r. data: τ 2.67 (s, 5 aromatic protons), 5.60 (t, 1 H, *J* 7 Hz, PhC*H*CH_2), 6.92 (d, 2 H, *J* 7 Hz, HCCH_2C=O), 7.20 (q, 2 H, *J* 8 Hz, CH_3CH_2SC=O), 7.67 (q, 2 H, *J* 8 Hz, SCH_2CH_3), and 8.85 (t, 6 H, *J* 8 Hz, 2 SCH_2CH_3). Continued elution afforded 5,6-*O*-isopropylidene-3-*O*-methyl-L-ascorbic acid (**15**; 0.1 g, 52%) having n.m.r. and i.r. spectra indistinguishable from those of an authentic sample.

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