The Structure of Leudrin, and the Nucleophilic Substitution of its Primary Hydroxy Group by Bromine

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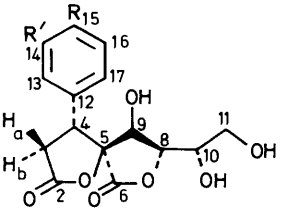
Leudrin (**1a**), present in some genera of the Proteaceae, is a pyrocatechol analogue of the phenolic spirobislactone leucodrin (**1b**). It has been characterized as its highly crystalline *ar*-dimethyl ether (**1c**). Leudrin can be re-formed from this derivative by demethylation with boron tribromide; under the conditions of the demethylation, it also undergoes unusual nucleophilic substitution to afford 11-bromo-11-deoxyleudrin (**5a**). The latter derivative affords leudrin after reaction with silver nitrate.

Leudrin (**1a**) is a pyrocatechol analogue of leucodrin (**1b**)[1,2] of known stereochemistry.[3] Leudrin accompanies leucodrin as a characteristic metabolite of the genera *Leucadendron*,[4] *Mimetes*,[5] *Sorocephalus*,[5] and *Spatalla*,[5] while conocarpin,[6] the

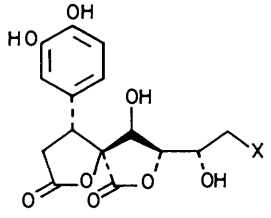


(**1a**) R = R′ = OH
(**1b**) R = OH, R′ = H
(**1c**) R = R′ = OMe
(**1d**) R = OMe, R′ = H

C-4 epimer of leucodrin, occurs in the genera *Leucospermum*,[4] *Diastella*,[5] *Orothamnus*,[5] *Paranomus*,[5] and *Serruria*[5] (all fam. Proteaceae). Leudrin has never been obtained in crystalline form, but its similarity to the leucodrin and conocarpin families of compounds was previously shown by the closely congruent ^{13}C and ^{1}H n.m.r. data for the crystalline *ar*-dimethyl ether (**1c**) and its trimethylsilyl ether derivative respectively.[7] We now present some of the structural chemistry of leudrin along with further spectroscopic studies.

Chemical characterization of leudrin showed the presence of five hydroxy groups through the formation of a penta-acetate. The aromatic substitution pattern was demonstrated by the oxidation (alkaline potassium permanganate) of leudrin *ar*-dimethyl ether (**1c**) to veratric acid. The chirality of C-4 in leudrin *ar*-dimethyl ether ($[\alpha]_D$ −20°) was established as *R* by oxidative degradation with sodium metaperiodate to the monohydrate of optically active 3,4-dimethoxyphenylsuccinic acid (**2**), ($[\alpha]_D$ −57°). The optical rotation of this enantiomer has not been reported hitherto; however, (*R*)-(−)-4-methoxyphenylsuccinic acid (**3**) obtained in the same manner from leucodrin *ar*-methyl ether (**1d**) has $[\alpha]_D$ −126°,[2] while its enantiomer (**4**) similarly obtained from conocarpin has $[\alpha]_D$ +127°.[6] The optical purity of the present preparation of the derived succinic acid (**2**) is not known, but its o.r.d. and c.d. spectra show negative Cotton effects (see Experimental section), as do the spectra of the (−)-4-methoxyphenyl analogue (**3**),[8] while the (+)-enantiomer (**4**) of the latter has positive Cotton effects at similar wavelengths.[9] The chirality of C-2 in (**2**) and of C-4 in leudrin *ar*-dimethyl ether (**1c**) is therefore *R*, and so also for leudrin (**1a**) if no change takes place during its methylation under alkaline conditions (see Experimental section). This proviso was verified by demethylating leudrin *ar*-dimethyl ether (**1c**) with boron tribromide,[10] *i.e.*, under acidic conditions.

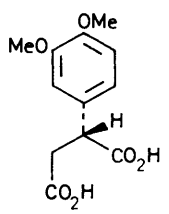
The boron tribromide-induced demethylation of aryl ethers involves co-ordination of the reagent to all Lewis base sites in the substrate.[11] In the case of leudrin *ar*-dimethyl ether (**1c**), this entails at least 7 mol equiv. of reagent. A reaction with 11 mol equiv. was found to afford partially demethylated products, while use of a large excess (50 mol equiv.) of reagent under more drastic conditions afforded total demethylation, and leudrin was obtained in 28% yield. At the same time, however, an



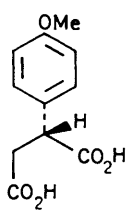
(**5a**) X = Br
(**5b**) X = ONO_2

unusual nucleophilic substitution of the 11-hydroxy group by bromine occurred to give 11-bromo-11-deoxyleudrin (**5a**) in 43% yield. Related substitutions of acetoxy groups by bromine under the influence of boron tribromide have been reported,[12] but replacement of a hydroxy group, as in this case, appears to be unprecedented. The regiospecificity of this substitution may here be attributed to the less hindered environment of the reagent-co-ordinated primary hydroxy group relative to that of the secondary hydroxy groups at C-9 and C-10.

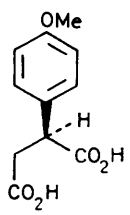
The structure of the bromo derivative (**5a**) could be demonstrated spectroscopically (see Tables 1—3 and Experimental section). Its structure was further confirmed by its reaction with silver nitrate in acetonitrile[13] (as contrasted with aqueous solvents) to give leudrin, characterized by paper



(**2**)



(**3**)



(**4**)

Table 1. ^{13}C Chemical shifts (δ, CD_3CN solution, p.p.m. from TMS) at 50.32 MHz

	2	3	4	5	6	8	9	10	11	12	13[a]	14[b]	15[b]	16[a]	17	OMe	
Leudrin (**1a**)[c,d]	174.45	33.47	41.57	89.76	171.93	80.33	69.92	69.21	61.97	125.16	115.44	144.59	144.75	115.71	120.95		
11-Bromo-11-deoxyleudrin (**5a**)[c]	174.34	33.26	41.59	89.74	171.62	79.81	69.87	68.22	32.60	124.90	115.46	144.64	144.75	115.61	120.88		
Leudrin *ar*-dimethyl ether (**1c**)[e]	174.40	33.29	41.72	89.74	171.94	80.34	69.89	69.19	61.89	125.45	111.52	148.99	149.24	112.42	121.09	55.23	55.32

Table 2. ^{1}H Chemical shifts (δ, CD_3CN solution, p.p.m. from TMS) at 200.13 MHz

	3a	3b	4	8	9	10	11a	11b	13	16	17	9-OH	10-OH	11-OH	ArOH	OMe	
Leudrin (**1a**)[c,d]	2.82	3.11	4.28	3.67	4.70	3.62	3.36	3.47	6.78	6.78	6.87	4.55	*ca.* 3.3	2.98	6.93		
11-Bromo-11-deoxyleudrin (**5a**)[c]	2.83	3.12	4.31	3.84	4.71	3.84	3.35	3.36	6.78	6.78	6.87	4.56	3.80		6.94		
Leudrin *ar*-dimethyl ether (**1c**)[e]	2.86	3.22	4.38	3.66	4.72	3.60	3.36	3.43	6.97	6.91[f]	6.92[f]	4.52	3.25	2.92		3.76	3.78

Table 3. Proton-proton coupling constants, $J_{H,H}$ (Hz)[g]

	3a, 3b	3a, 4	3a, 9	3b, 4	8, 9	8, 10	10, 11a	10, 11b	11a, 11b	16, 17	9, OH	10, OH	11a, OH	11b, OH
Leudrin (**1a**)	−17.6	8.8	1.0	12.6	8.5	2.9	6.8	6.0	−10.8	1.2	5.0	—	*ca.* 5	*ca.* 5
11-Bromo-11-deoxyleudrin (**5a**)	−17.4	8.8	0.8	12.8	8.0	—	*ca.* 6	*ca.* 6	—	1.4	—	—		
Leudrin *ar*-dimethyl ether (**1c**)	−17.5	8.9	0.8	12.6	8.5	2.9	6.4	6.0	−11.2	3.1	5.2	—	6.4	5.2

[a,b] The values for 13/16 and for 14/15 can be interchanged. [c] Solution degassed. [d] This sample of leudrin was obtained by demethylation of pure leudrin *ar*-dimethyl ether. [e] Solution not degassed. [f] These values can be interchanged. [g] A dash (—) in Table 3 indicates that couplings were not observed or were not clearly resolved.

chromatography, silylation—g.l.c., and mass spectrometry. The leudrin so formed was accompanied by a minor product identified as leudrin 11-nitrate (**5b**), which is therefore a likely intermediate in these silver-cation mediated nucleophilic substitution reactions.

The ^{13}C resonances in Table 1 were assigned with the help of data reported for the trimethylsilyl ether derivative of leudrin *ar*-dimethyl ether (**1c**),[7] and for simpler pyrocatechol derivatives.[14] In the case of 11-bromo-11-deoxyleudrin (**5a**), the signal at 61.97 p.p.m. (C-11) in the leudrin spectrum was not observed, but a new signal consistent with a primary alkyl bromide[15] was found at 32.60 p.p.m. For all three compounds in Table 1, the difference between the chemical shifts of the aromatic carbons 13 and 16, and also of 14 and 15, was less than 1 p.p.m., and no attempt was made to distinguish between them. Spectra were obtained from *ca.* 20 000 transients.

The ^1H n.m.r. data in Tables 2 and 3 were obtained by means of correlated (COSY) and *J*-resolved (JRES) experiments as well as selective homodecoupling. A feature of interest in the spectra of the three compounds concerned is a long-range interaction between protons 3a and 9 (^5J = 1.0 or 0.8 Hz). Dreiding models of the compounds show that these interacting nuclei can adopt an 'extended W' arrangement, reported *J* values for which are as large as 2.3 Hz.[16] That such an interaction is observed here suggests puckering of the two lactone rings in a fashion that allows for near-coplanarity of the five bonds over which coupling extends.

It should be mentioned that the hydroxy resonances observed in the spectrum of a freshly prepared, degassed solution of leudrin (**1a**) disappeared after the solution had been left at room temperature for *ca.* 5 h. In the case of the bromo derivative (**5a**) (solution degassed) and leudrin *ar*-dimethyl ether (**1c**) (solution not degassed), the hydroxy signals were unchanged after four days. The reasons for these observations are not clear.

Experimental

Routine measurements were taken on a Kofler micro hot-stage (m.p.) apparatus, Perkin-Elmer 521 and Pye-Unicam SP3-300 (i.r. in KBr dispersion), AEI MS-9 and Varian-MAT CH7 (m.s.), Hitachi-Perkin-Elmer R20, Varian HA-100, and Bruker AC200 FT (n.m.r.) spectrometers, a Jasco ORD/UV-5 spectrophotometer with c.d. attachment (o.r.d. and c.d.), a Perkin-Elmer 241B polarimeter (optical rotations), and a Pye-Unicam GCD gas chromatograph (g.l.c.). T.l.c. was on pre-coated silica gel plates (Merck F254). Analytical g.l.c. was over a column (2.1 × 0.002 m) of OV17 (1% on Anakrom Q) with nitrogen as the carrier gas at 26 ml min^{-1}; all runs were programmed at 8 °C min^{-1}, injector and detector ports were at 300 °C, and emergent temperatures were read from the oven thermometer and are recorded as ET_{222} for a starting temperature of 222 °C. Runs were standardized against cholesterol (ET_{222} 267 °C) either internally or externally. Samples (1 mg) for silylation were kept in 0.1 ml of bistrimethylsilyltrifluoroacetamide–pyridine (1 : 1, v/v) for 2 h at 73 °C. Product distributions were calculated from peak heights.[17] Reversed phase paper chromatography (p.c.) was on Whatman 2 paper impregnated with glycerol and eluted with butanol–toluene (1 : 1, v/v) saturated with water;[4] hR_L relates to leucodrin as reference.

Leudrin.—Milled dried leaves (1 kg) of *Mimetes cucullatus* (L.) R. Br.* were extracted (Soxhlet) with methanol for 30 h. The dried extract (109 g) was chromatographed over silica gel in benzene–ethyl acetate–methanol mixtures; the leudrin-rich (t.l.c.) fractions were rechromatographed twice more to yield leudrin (**1a**) as a colourless foam (3.5 g); p.c. hR_L 50,[4] silylation–g.l.c. ET_{222} 258 °C; $\bar{\nu}_{max.}$ 3 400 br (OH), 1 780 (C=O), and 1 600 and 1 520 cm^{-1} (aromatic).

Leudrin Penta-acetate.—Leudrin (**1a**) (170 mg) was kept in pyridine–acetic anhydride (4 ml of each) and left at room temperature for 70 h. Chromatography over silica gel yielded a glass (185 mg) of *leudrin penta-acetate*, purified by distillation at 155 °C/10^{-5} Torr (Found: C, 54.65; H, 4.75. $C_{25}H_{26}O_{14}$ requires C, 54.55; H, 4.74%); $\bar{\nu}_{max.}$(film) 3 010 (ArH), 1 800 and 1 750 (C=O), 1 500 and 1 430 (aromatic), 1 210 (C–O–C), and 750 cm^{-1}; δ (100 MHz, $CDCl_3$) 7.3 (3 H, m, ArH), 5.80 (1 H, d, *J* 8.1 Hz, 9-H), 5.13 (1 H, td, *J* 6.1 and 2.0 Hz, 10-H), 4.17, 4.10, and 3.95 (4 H superimposed; dd, *J* 13.0 and 8.2 Hz, 4-H; d, *J* 5.7 Hz, 2 × 11-H; and dd, *J* 8.1 and 2.0 Hz, 8-H), 3.27 (1 H, dd, *J* −17.2 and 13.0 Hz, 3b-H), 2.87 (1 H, dd, *J* −17.2 and 8.2 Hz, 3a-H), 2.26 (6 H, s), 2.24 (3 H, s), 2.10 (3 H, s), and 1.93 (3 H, s) (all $OCOCH_3$); *m/z* 550 ($[M]^+$, 1), 508 (3), 466 (17), 424 (15), 382 (6) (all successive losses of ketene), and 149 (100%).

Leudrin Ar-*Dimethyl Ether* (**1c**).—Leudrin (1.02 g) in water (15 ml) was treated with dimethyl sulphate (4.5 ml) and 50% aqueous potassium hydroxide (6.5 ml). The solution was deaerated by passage of nitrogen gas, kept at room temperature for 48 h, acidified with hydrochloric acid, and heated at 60 °C for 1 h. After neutralization with ammonia liquor and drying, the residue was extracted with methanol and the dried extract chromatographed over silica gel with benzene–ethyl acetate–methanol mixtures. Combined (t.l.c.) fractions afforded *leudrin* ar-*dimethyl ether* (**1c**) (229 mg), m.p. 224—225 °C (from MeOH), m.p. 216 °C (from water) (Found: C, 55.55; H, 5.45. $C_{17}H_{20}O_9$ requires C, 55.44; H, 5.44%) (Found: M^+, 368.109. $C_{17}H_{20}O_9$ requires M^+, 368.111); silylation-g.l.c. ET_{222} 263 °C (100%); $[\alpha]_D$ −20° (MeOH, *c* 0.2); $\bar{\nu}_{max.}$ 3 420 and 3 240br (OH), 1 775 (C=O), 1 580, 1 510, and 1 430 cm^{-1} (Ar); *m/z* 368 (M^+, 55) and 164 (100%); n.m.r. data are in Tables 1—3.

(−)-3,4-*Dimethoxyphenylsuccinic Acid Hydrate* (**2**).—Leudrin *ar*-dimethyl ether (118 mg) in aqueous sodium hydroxide (0.44M; 9 ml) was treated with sodium metaperiodate (900 mg) in water (10 ml) at pH > 5. The mixture was heated at 40 °C for 4 h, cooled, and treated with ice (10 g) followed by an excess of sulphur dioxide gas. Continuous extraction with ether (16 h) yielded an extract (98 mg) which was chromatographed twice over silica gel in benzene–acetone–acetic acid mixtures to yield (t.l.c.) (−)-3,4-*dimethoxyphenylsuccinic acid* (**2**) *hydrate* (16 mg), double m.p. 135 °C and 172—175 °C (from water) (lit.,[18] m.p. 126—128 °C for hydrate, m.p. 172—174 °C for anhydrous compound) (Found: M^+, 254.078. $C_{12}H_{14}O_6$ requires M^+, 254.160); $[\alpha]_D$ −57° (50% aqueous ethanol, *c* 0.08); o.r.d. [Φ]/nm −930°/248, −170°/278, −240°/280, −170°/285, −230°/290, and c.d. (Δε/nm) −1.1/250, −0.5/278, 0/290, both in methanol (*c* 0.24) solution; $\bar{\nu}_{max.}$ 3 480 and 2 940br (CO_2H), 1 725sh and 1 700 (C=O), 1 590 and 1 515 (Ar), and 1 260 cm^{-1} (C–O–C); δ[60 MHz, $(CD_3)_2CO$] 6.9 (3 H, m, ArH), 4.0 (1 H, dd, *J* 10 and 4 Hz, 2-H), 3.81 and 3.79 (6 H, 2 s, 2 OMe), 3.1 (1 H, dd, *J* −17 and 10 Hz, 3a-H), and 2.7 (1 H, dd, *J* −17 and 4 Hz, 3b-H); *m/z* 254 (M^+, 18), 236 (65), 208 (26), and 164 (100%).

Veratric Acid.—The combined residues from the foregoing experiment (70 mg) and potassium hydroxide (160 mg) in water (4 ml) were boiled, and potassium permanganate (240 mg) in water (6 ml) was added over 1 h. The solution was cooled, treated with an excess of sulphur dioxide gas until it was clear, and then continuously extracted with ether. The dried extract

* Authentic control samples were provided by Dr. J. P. Rourke, Curator, Compton Herbarium, National Botanic Gardens of South Africa, Kirstenbosch.

was evaporated and the residue chromatographed over silica gel to afford veratric acid (16 mg), m.p. and mixed m.p. 179—183 °C, and i.r. spectrum identical with that of an authentic specimen.

Demethylation of Leudrin Ar-*Dimethyl Ether*.—(*a*) Leudrin *ar*-dimethyl ether (**1c**) (30 mg, 0.082 mmol) as a dried insoluble film under dichloromethane (10 ml) was treated with boron tribromide (220 mg, 0.88 mmol) in dichloromethane (1 ml) under nitrogen at 0 °C for 30 min. The clear solution was evaporated under reduced pressure and the residue quenched with water. Polar products were obtained, by continuous extraction with ether (24 h), as a gum (26 mg) which on silylation-g.l.c. showed three components with ET_{222} 258 °C (leudrin), 260 °C, and 263 °C (leudrin *ar*-dimethyl ether). The silylation product with ET_{222} 260 °C could be that of a leudrin *ar*-monomethyl ether. (*b*) Leudrin *ar*-dimethyl ether (**1c**) (20.4 mg, 0.054 mmol as above) was stirred under dichloromethane (7 ml) and treated with boron tribromide (680 mg, 2.71 mmol) in dichloromethane (1.5 ml) under nitrogen at 0 °C for 20 min; the mixture was then kept at 24 °C for 16 h. After evaporation under reduced pressure the residue was quenched with water (5 ml) and hydrochloric acid (10M; 5 ml) and the solution was kept at 80 °C for 5 h to relactonize any opened hydroxy acids. Continuous extraction with ether (18 h) afforded a residue which was leached with methanol to yield a soluble gum (23 mg) which was chromatographed over silica gel (20 g) in benzene–ethyl acetate–methanol (5:1:1, v/v). Two phenolic products (Pauly spray reagent) were clearly separated (t.l.c. hR_F 28 and 53 in benzene–ethyl acetate–methanol, 3:1:1 v/v), and combined fractions afforded the following. (*i*) The low-R_F product as a gum (5.1 mg, 0.015 mmol, 28% yield) identified as leudrin by silylation-g.l.c. (Found: M^+, 700.265. $C_{30}H_{56}O_9Si_5$ requires M^+, 700.277); ET_{222} 258 °C (99% purity) and 264 °C (1%); by p.c. hR_L 50; and by $\bar{\nu}_{max.}$ 3 400br (OH), 1 780 (C=O), 1 600 and 1 520 (Ar), 1 380 (prim. OH), and 1 110 cm^{-1} (sec. OH)[19] as for leudrin; n.m.r. data for this sample are in Tables 1—3. (*ii*) The high-R_F product as a gum (9.4 mg, 0.023 mmol, 42% yield) identified as 11-*bromo*-11-*deoxyleudrin* (**5a**). It gave a strongly positive Beilstein test for halogen and showed p.c. hR_L 150; and $\bar{\nu}_{max.}$ 3 400br (OH), 1 780 (C=O), 1 600 and 1 520 (Ar), and 1 110 cm^{-1} (sec. OH) with no peak at 1 380 cm^{-1} (prim. OH); n.m.r. data are in Tables 1—3. Its silylation product (Found: M^+, 690.153. $C_{27}H_{47}{}^{79}BrO_8Si_4$ requires 690.151) showed ET_{222} 265 °C (97% purity) and 260 °C (3%).

Conversion of 11-*Bromo*-11-*deoxyleudrin* (**5a**) *into Leudrin*.—Trials with silver acetate in acetic acid, and with potassium hydroxide in aqueous alcoholic medium were unsuccessful in this respect. Effective conversion was achieved by keeping (**5a**) (0.8 mg) in a solution (0.5 ml) of silver nitrate [4% in aqueous acetonitrile (40% water)] without a precipitate forming over 24 h. The solution was evaporated under reduced pressure and the residue (20 mg) was dissolved in undried acetonitrile (0.5 ml), when a white precipitate of silver bromide formed immediately and turned grey in daylight. After 30 min, water (0.3 ml) was added, and the mixture was kept for 15 min prior to the addition of sodium chloride (13 mg) in water (0.13 ml). The mixture was dried *in vacuo* and the residual salts leached with absolute ethanol (1 ml) to obtain the products. The product mixture showed p.c. hR_L 140 for unchanged bromide (**5a**) and hR_L 50 for leudrin. A silylated sample showed (*a*) ET_{222} 259 °C (75%) and *m/z* 700 for silylated leudrin ($C_{30}H_{56}O_9Si_5$); (*b*) ET_{222} 265 °C (22%) and *m/z* doublet at 690/692 for silylated unchanged 11-bromo-11-deoxyleudrin ($C_{27}H_{47}BrO_8Si_4$); and (*c*) a small peak at ET_{222} 251 °C (3%) ascribed to *leudrin* 11-*nitrate* (**5b**) on the basis of its composition (Found: M^+, 673.210. $C_{27}H_{47}NO_{11}Si_4$ requires M^+, 673.222) for the silylated derivative.

Acknowledgements

We thank the Foundation for Research Development for financial assistance (J. P. M.), the Council for Scientific and Industrial Research for spectra, and Dr. P. R. Boshoff (m.s.) and Mrs. S. Heiss (n.m.r.) for their dedicated and able support.

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Received 14*th April* 1987; *Paper* 7/669