Phytochemistry, Vol. 22, No. 4, pp. 975–978, 1983.
Printed in Great Britain.

0031–9422/83/040975–04$03.00/0

SECOIRIDOID AND TRITERPENIC ACIDS FROM THE STEMS OF *NAUCLEA DIDERRICHII*

ADEBOWALE O. ADEOYE and ROGER D. WAIGH

Department of Pharmacy, University of Manchester, Manchester, M13 9PL, U.K.

(*Received* 22 *June* 1982)

Key Word Index—*Nauclea diderrichii*; Rubiaceae; alkanes; alkanoic acids; triterpenic acids; secoiridoid; quinovic acid; 3-oxoquinovic acid; 3-*O*-glucosylquinovic acid; diderroside.

Abstract—The stem bark of *Nauclea diderrichii* has yielded diderroside, a new secoiridoid glucoside, as well as quinovic acid, 3-oxoquinovic acid and 3-*O*-glucosylquinovic acid. The hydrocarbon fraction was dominated by *n*-heptacosane and *n*-nonacosane, which accords with the predominance of *n*-octacosanoic acid in the alkanoic acid fraction.

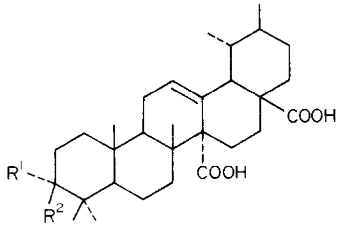
INTRODUCTION

Nauclea diderrichii (De Wild) Merr. (*Sarcocephalus diderrichii* De Wild) is a large evergreen tree abundant in the rain forests of West Africa. The bark finds some local use in the treatment of gonorrhoea, for stomach pains, fever and sometimes diarrhoea. Its strength as a timber and resistance to termites make it valuable in construction work, although sawmill workers have been reported to suffer from cardiac poisoning associated with its use [1].

Previous work on *N. diderrichii* has yielded a number of alkaloids [2–7], some of which may be artefacts [8]. Our own results with the alkaloids will be reported separately. The non-alkaloidal constituents reported by other workers include naucleol, antiarol and the secoiridoid naucledal [7] and, somewhat earlier, 'sitosterol palmitate', *meso*-inositol and *O*-methyl-*meso*-inositol from the heartwood [9]. Our analysis of the sterol ester mixture from the stem bark has been reported previously [10].

RESULTS AND DISCUSSION

Extraction of the powdered bark with petrol, followed by CC, gave four fractions, identified as hydrocarbons, sterol esters [10], sterols and fatty acids. The sterols proved to be an unexceptional mixture of sitosterol, stigmasterol and campesterol. The hydrocarbons were mainly normal alkanes, the most abundant being *n*-heptacosane, followed by *n*-nonacosane. This pattern was reflected in the alkanoic acids, of which the most abundant was *n*-octacosanoic acid. The relative abundancies of the alkanes and alkanoic acids may be of some chemotaxonomic value since they are certainly easier to isolate and identify, using GC/MS, than more complex metabolites.



1a $R^1 = OH$, $R^2 = H$
1b $R^1 = R^2 = O$
1c $R^1 = Oglu$, $R^2 = H$

Chloroform extraction gave further amounts of the four types of mixture obtained from the petrol extract. More polar fractions yielded two triterpenic acids tentatively identified from mass spectral and NMR data as quinovic acid (**1a**) [11] and the rarely reported [12] 3-oxoquinovic acid (**1b**). These were separated by prep. TLC as their methyl esters, one of which was shown to be identical to a sample of quinovic acid obtained elsewhere, and similarly methylated. The latter sample also contained 3-oxoquinovic acid, which may indicate that it is more common than supposed. The 3-oxoquinovic acid dimethyl ester was converted to quinovic acid dimethyl ester on reduction with sodium borohydride by analogy with the reduction of 3-oxocadambagenic acid dimethyl ester described by previous workers [11]. An even more polar fraction from this extract was shown to contain quinovic acid 3-*O*-glucoside (**1c**), purified and characterized as the dimethyl ester tetra-acetate. This glucoside was first reported from the Rubiaceae [13].

The water-soluble part of the chloroform extract contained small quantities of a substance later designated WF2A, larger amounts of which were present in the methanol extract. The water-soluble portion of the latter was subjected to charcoal-CC to remove sugars, and then gave a fraction which HPLC showed to contain a complex mixture. One component of the mixture was separated as a pure compound by semi-prep. HPLC, and called WF2A, identical to the smaller amount of material isolated from the chloroform extract. Experience showed WF2A to possess limited stability in solution, but sufficient data were obtained on samples soon after purification to allow structure elucidation.

The UV spectrum of WF2A showed absorption at 234 nm, typical of the O–C=C–COOMe system of iridoids [14]. This suggestion was supported by the ^1H NMR spectrum which showed a one-proton singlet at $\delta 7.55$ (H-3) and a three-proton singlet at 3.71 (COOMe-4). A three-proton singlet at 2.07 suggested an acetyl group, and a three-proton doublet ($J = 7$ Hz) at 1.40 correlated well with a methyl group with a hydroxyl or acetoxy group on the neighbouring carbon atom. Other signals provisionally assigned were a doublet ($J = 8$ Hz) at 5.80 (H-1) and a one-proton multiplet at 5.25 (H-8) which suggested that an acetoxy group was attached at C-8 as well as the C-10 methyl. There was a doublet at 4.80 ($J = 7$ Hz) for the anomeric proton of a sugar, for the remaining protons of which there was complex absorption in the region 3.3–4.08. Other separated resonances assigned subsequently were a two-proton doublet ($J = 7$ Hz) at 2.33 and a multiplet for one proton at 2.20.

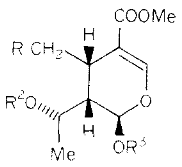
Hydrolysis with β-glucosidase showed that the sugar was β-D-glucose, although we could not isolate the aglucone, and the presence of a β-glucoside was confirmed by the ^{13}C NMR spectrum, which showed the characteristic resonances [15] at 99.7, 77.2, 76.7, 73.7, 70.8 and 61.9. Other resonances confirmed the iridoid skeleton [14], with C-1 at 97.2, C-3 at 154.2, C-4 at 110.4, C-11 at 169.6, methoxy at 52.6 and C-10 methyl at 19.1. The acetoxy group was confirmed by resonances at 21.8 and 174.0. Other signals, consistent with a secoiridoid structure and subsequently assigned, were located at 70.5 (C-8), 43.6 (C-9) and 29.6 (C-5). A broadened signal at 36.4, a triplet in the off-resonance spectrum, was assigned to C-6 which left C-7 unaccounted for.

At this stage we were able to make a tentative structure assignment as **2a**, excluding C-7, and sought further evidence from mass spectrometry. However, even direct probe insertion with chemical ionization failed to give a molecular ion. This problem was overcome with field desorption, which indicated a MW of 464, and this was confirmed by desorption–chemical ionization [16], the latter technique giving the simplest spectrum. With a consideration of the previous data, the missing carbon had to be part of a carboxylic acid group, so that in the ^{13}C NMR spectrum it may have been superimposed on one of the other carbonyl carbons; shortage of material has prevented confirmation of this by changing solvent. The broadening of the C-6 signal may also have been reflected in broadening of the C-7 signal, if the former was attributable to conformational changes caused by alternate hydrogen bonding to ester groups on either side, and may have obscured the presence of the C-7 signal.

It was apparent that WF2A was a secoiridoid, previously unknown, to which we gave the name 'diderroside', and allocated structure **2a**. Acetylation gave diderroside tetra-acetate (**2b**), previously known as a synthetic intermediate [17], for which the ^{1}H NMR spectrum was consistent with the proposed structure. Methylation of the tetra-acetate with diazomethane confirmed the presence of the free carboxylic acid group, with a second methoxy signal in the ^{1}H NMR spectrum, and gave a product (**2c**) with sufficient volatility to allow accurate mass measurement of the molecular ion ($C_{26}H_{35}O_{15}$) and several fragments.

As final confirmation of the structure a series of decoupling experiments was carried out on methyl diderroside tetra-acetate (**2c**) at 300 MHz, which allowed assignment of all the resonances.

The question of the relative stereochemistry of diderroside (**2a**) was fortunately solved by the very recent structure elucidation [18] of alpigenoside (**2d**), for which the stereochemistry has been defined by conversion to tetra-acetylkingiside (**3**), of known absolute configuration [17]. Comparison of diderroside tetra-acetate methyl ester with penta-acetylalpigenoside by TLC and 300 MHz NMR showed that diderroside is des-7-O-methyl-8-O-acetylalpigenoside, with all four secoiridoid asymmetric centres in the same relative configurations. Shortage of material prevented measurement of the optical rotation of methyldiderroside tetra-acetate which, by comparison with the measured rotation of penta-acetylalpigenoside [18], would confirm the absolute stereochemistry. However, it is highly improbable that diderroside has a different absolute stereochemistry from alpigenoside.

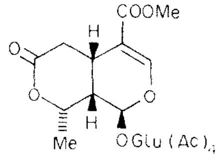


2a R^1 = COOH, R^2 = MeCO, R^3 = Glu

2b R^1 = COOH, R^2 = MeCO, R^3 = Glu $(Ac)_4$

2c R = COOMe, R^2 = MeCO, R^3 = Glu $(Ac)_4$

2d R^1 = COOMe, R^2 = H, R^3 = Glu



3

EXPERIMENTAL

Plant material was collected from a forest reserve on the Benin–Ijebu-Ode road, Nigeria and identified by Mr. Daramola, senior plant collector of the Forestry Research Institute of Nigeria. This identification was confirmed by comparison with voucher specimens at the institute's herbarium. Herbarium specimens have been deposited with the University of Manchester Museum.

Extraction and separation. The powdered stem bark (4 kg) was extracted with cold petrol (bp 40–60°, 10 l., 2 × 5 l.) for 48 hr each time. The combined residue (9.13 g) was extracted with $CHCl_3$ to give a sticky residue (33 g). The MeOH extract of the stem bark was a brown powder (370 g). The powdered heartwood (4 kg) was extracted only with cold MeOH (15 l., 3 × 6 l.) to give 217 g of a brown powder.

The petrol extract (6 g) was chromatographed on a Si gel column, eluting with petrol (bp 60–80°) with increasing proportions of $CHCl_3$ to yield an alkane fraction (1.70 g), steryl esters (0.42 g), sterols (2.00 g) and fatty acids (0.33 g). The $CHCl_3$ extract (20 g) was extracted with petrol to give 7.25 g of material similar to the petrol extract. The petrol insoluble material was further divided into H_2O soluble (1.54 g) and H_2O insoluble (7.85 g) material. The H_2O-insoluble residue (2 g) was chromatographed on Si gel using petrol, petrol–$CHCl_3$ and $CHCl_3$–MeOH to give (with 5% MeOH in $CHCl_3$) a mixture of quinovic acid and 3-oxoquinovic acid (340 mg). Elution with 10% MeOH in $CHCl_3$ gave 3-O-glucosyl-quinovic acid (90 mg).

The MeOH extract (250 g) was extracted with H_2O to give a brown gum (110 g). This material (25 g) was chromatographed on a prepared charcoal column, eluting first with H_2O and then with aq. MeOH (5–40%). Fractions obtained with 20–30% MeOH were bulked and evaporated at 30–40° *in vacuo* to give a yellow powder (1.52 g) which gave negative tests for reducing sugars. This powder was dissolved in 10% MeCN and chromatographed in 100 μl aliquots on a semi-prep. HPLC column, eluting with 10% MeCN and detecting at 254 nm. Fractions containing the major component were combined and freeze-dried to give a light off-white powder (46 mg) which undoubtedly represented only a small part of the material originally present, but was pure by analytical HPLC.

The only non-alkaloidal component isolated from the heartwood was *O*-methylinositol, which has previously been reported from this species [9].

Hydrocarbons. GC/MS using a 1% Dexsil 300 column, temp. programmed at 100° for 2 min followed by a rise of 8°/min to 250° gave the following percentages (chain lengths): *n*-alkanes 0.1 (14), 1.0 (15), 2.9 (16), 5.0 (17), 4.2 (18), 1.7 (19), 2.8 (20), 2.5 (21), 2.7 (22), 3.1 (23), 2.7 (24), 7.5 (25), 2.9 (26), 30.5 (27), 4.3 (28), 13.7 (29), 7.0 (30), 3.5 (31), 1.8 (32); *n*-alkenes C_{17}–C_{27}, *iso*-alkanes C_{17}–C_{25}, none greater than 0.3%.

Alkanoic acids. These showed the expected carbonyl absorption at 1705 cm^{-1} and ^1H NMR absorption at δ9.8 (*br s*, COOH), 1.25 [*br s*, $(CH_2)_n$] and 0.9 (*t*, Me). Methylation with BF_3–MeOH complex gave the methyl esters, with IR absorption at 1748 cm^{-1} and an additional ^1H NMR spectral peak at δ3.65 (OMe). GC/MS using a 1% Dexsil 300 column programmed at 150° for 2 min and a rise of 10°/min to 270° gave the following percentages (chain lengths): 10.1 (16), 13.6 (18, Δ1), 9.0 (18), 3.2 (24), 16.0 (26), 2.1 (27), 39.8 (28), 6.0 (30).

Quinovic acid and 3-*oxo-quinovic acid.* The mixture of these two components obtained by chromatography had mp 267° (decomp.) and showed IR carbonyl absorption at 1695 cm^{-1}; ^1H NMR (80 MHz, DMSO-d_6): δ12.1 (*br*, COOH), 5.5 (*br s*, H-12), 3.3 (*br m*, H-3), 0.8–0.9 (*m*, Me). Separation of the acids was not feasible, so the mixed acids were methylated with CH_2N_2 and separated by prep. TLC on Si gel, developing with $CHCl_3$–C_6H_6 (9:1). From 100 mg of crude mixed acids was obtained 27 mg dimethyl quinovate and 40 mg dimethyl 3-oxoquinovate. Each was crystallized from petrol (bp 40–60°) and then from petrol containing a small amount of MeOH. Dimethyl quinovate had mp 163–165° (lit. [19–21] 169–171°, 179.5–181°, 174–176°) $[\alpha]_D$ +73.3° ($CHCl_3$; *c* 1.76), IR ν_{max} cm^{-1}: 3650, 1720, 1700; ^1H NMR (300 MHz, $CDCl_3$): δ5.66 (1H, *t*, J = 2 Hz, H-12), 3.62 (3H, *s*, COOMe), 3.61 (3H, *s*, COOMe), 3.19 (1H, *q*, J = 6 Hz, H-3), 0.91 (3H, *d*, Me), 0.87, 0.85, 0.83, 0.74 (12H, 4*s*, 4 × Me), 0.82 (3H, *d*, Me); EIMS 70 eV, *m*/*z* (rel. int.): 514.3624 (13.7), calc. for $C_{32}H_{50}O_5$; 514.3645 $[M]^+$, 496.3442 (2.6), calc. for $C_{32}H_{48}O_4$; 496.3552 $[M - H_2O]^+$, 395.3402 (6.0), calc. for $C_{28}H_{43}O$; 395.3314 $[M - 2 \times COOMe - H]^+$, 306.1810 (26.7), calc. for $C_{18}H_{26}O_4$; 306.1831 $[M - C_{14}H_{24}O]^+$, 207.1748 (100), calc. for $C_{14}H_{25}O$; 207.1749 $[M - C_{18}H_{25}O_4]^+$, 190.1724 (74.2), calc. for $C_{14}H_{22}$; 190.1721 $[M - H_2O - C_{18}H_{24}O_4]^+$. Prominent ions not accurately mass measured were 482 $[M - 32]^+$ (24.3), 464 $[M - 50]^+$ (3.8), 455 $[M - 59]^+$ (17.2), 328 $[M - 186]^+$ (6.9), 274 $[M - 240]^+$ (62.8), 247 $[M - 267]^+$ (50.9). (Found: C, 74.2; H, 9.8. Calc. for $C_{32}H_{50}O_5$: C, 74.6; H, 9.8%.)

Dimethyl 3-oxoquinovate had mp 144–144.5° (lit. [12] 156–157°), $[\alpha]_D$ +98.0° ($CHCl_3$; *c* 1.00), IR ν_{max} cm^{-1}: 1720, 1690, ^1H NMR (300 MHz, $CDCl_3$): δ5.69 (1H, *t*, H-12), 3.64 (6H, *s*, 2 × OMe), 2.5 (2H, *m*, H-2), 0.83–1.04 (18H, 2*d*, 4*s*, 6 × Me). EIMS 70 eV, *m*/*z* (rel. int.): 512.3492 (27.4), calc. for $C_{32}H_{48}O_5$; 512.3502 $[M]^+$, 453.3368 (57.5); calc. for $C_{30}H_{45}O_3$; 453.3369 $[M - COOMe]^+$, 306.1834 (23.5), calc. for $C_{18}H_{26}O_4$; 306.1831 $[M - 206]^+$, 274.1565 (45.0), calc. for $C_{17}H_{22}O_3$; 274.1569 $[M - 238]^+$. Prominent ions not accurately mass measured were 480 $[M - 32]^+$ (67.4), 421 $[M - 91]^+$ (11.3), 393 $[M - 129]^+$ (25.9), 262 $[M - 250]^+$ (17.7), 247 $[M - 265]^+$ (35.3), 215 $[M - 297]^+$ (46.7), 205 $[M - 307]^+$ (38.9), 128 $[M - 384]^+$ (20.2), 105 $[M - 407]^+$ (33.1), 91 $[M - 421]^+$ (50.4), 55 $[M - 457]^+$ (62.3), 41 $[M - 471]^+$ (100). (Found: C, 75.1; H, 9.7. Calc. for $C_{32}H_{48}O_5$: C, 75.0; H, 9.4%.)

A sample of quinovic acid (see acknowledgements) was found, after methylation, to give two spots on TLC, corresponding to dimethyl quinovate and dimethyl 3-oxoquinovate, in three solvent systems.

Dimethyl 3-oxoquinovate was converted to dimethyl quinovate (mp, mmp, TLC) by reduction in MeOH with $NaBH_4$.

3-O-*Glucosyl-quinovic acid.* This compound was difficult to purify and characterize owing to poor solubility in most solvents and lack of mobility on TLC. The dimethyl ester tetra-acetate was obtained as a white powder after prep. TLC on Si gel using $CHCl_3$–MeOH (4:1), and had mp 117–120°, broad IR band at 1750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ5.7 (1H, *m*, H-12), 5.6 (1H, *d*, J = 8 Hz, H-1′), 4.1–5.3 (5H, *m*, H-2′, H-3′, H-4′, H-5′ and H-6′), 3.65 (3H, *s*, COOMe), 3.63 (3H, *s*, COOMe), 2.0–2.14 (12H, 4*s*, 4 × COMe), 0.78–0.98 (18H, *m*, 6 × Me). EIMS 70 eV *m*/*z* (rel. int.): 496.3663 (1.5), calc. for $C_{32}H_{48}O_4$; 496.3552 [M − glucose tetra-acetate]$^+$, 331.1083 (8.7), calc. for $C_{14}H_{19}O_9$; 331.1029 [M − dimethyl quinovate]$^+$, 271.0890 (1.9), calc. for $C_{12}H_{15}O_7$; 271.0818 [M − dimethyl quinovate − MeCOOH]$^+$, 190.1746 (7.2) calc. for $C_{14}H_{22}$; 190.1721 [M − glucose tetra-acetate − $C_{18}H_{24}O_4$]$^+$, 169.0508 (24.7), calc. for $C_8H_9O_4$; 169.0501 [acetylated glucose fragment]$^+$. No molecular ion was observed; the base peak was at *m*/*z* 43. Acid hydrolysis gave glucose (identified by PC) and, after remethylation with CH_2N_2, dimethyl quinovate, identified by comparison with an authentic sample.

Diderroside. This compound was obtained as a white amorphous powder with no discrete mp. $[\alpha]_D$ −34.6° (MeOH; *c* 1.16), CD (MeOH; *c* 0.40) $\Delta\varepsilon_{220}$ −4.18, $\Delta\varepsilon_{249}$ +0.47, UV λ_{max}^{MeOH} nm (log ε): 234 (3.91), IR ν_{max}^{KCl} cm^{-1}: 3400, 1700. ^1H NMR (300 MHz, D_2O): δ7.55 (1H, *s*, H-3), 5.8 (1H, *d*, J = 8 Hz, H-1), 5.25 (1H, *m*, H-8), 4.8 (1H, *d*, J = 8 Hz, H-1′), 3.71 (3H, *s*, COOMe), 3.3–4.08 (7H, *m*, H-2′, H-3′, H-4′, H-5′, H-6a′, H-6b′, H-5), 2.33 (2H, *d*, J = 7 Hz, H-6), 2.2 (1H, *m*, H-9), 2.07 (3H, *s*, COMe), 1.4 (3H, *d*, J = 7 Hz, H-10). ^{13}C NMR (25.1 MHz, D_2O): δ174.0 (*s*, COMe), 169.6 (*s*, C-11), 154.2 (*d*, C-3), 110.4 (*s*, C-4), 99.7 (*d*, C-1′), 97.2 (*d*, C-1), 77.2 (*d*, C-5′), 76.7 (*d*, C-3′), 73.7 (*d*, C-2′), 70.8 (*d*, C-4′), 70.5 (*d*, C-8), 61.9 (*t*, C-6′), 52.6 (*q*, OMe), 43.6 (*d*, C-9), 36.4 (*t*, C-6), 29.6 (*d*, C-5), 21.8 (*q*, MeCO), 19.1 (*q*, C-10). FDMS *m*/*z* (rel. int.): 487 $[M + Na]^+$ (100), 469 $[M - 18 + Na]^+$ (12.5), 464 $[M]^+$ (10.0), 446 $[M - 18]^+$ (6.0), 437 $[M - 27]^+$ (7.2), 406 $[M - 58]^+$ (15.7). DCI (NH_3) *m*/*z* (rel. int.): 464 $[M]^+$ (4.0), 447 $[M + H - H_2O]^+$ (4.0), 422 $[M + H - 43]^+$ (3.7), 405 $[M - 59]^+$ (1.6), base peak 180 [glucose]$^+$. A small sample of diderroside was hydrolysed with β-glucosidase in aq. soln, freeze-dried and chromatographed on paper to confirm glucose as a hydrolysis product. A further small sample was acetylated with Ac_2O–pyridine and the product purified by prep. TLC on Si gel using $CHCl_3$–MeOH (4:1) and obtained as a gum; ^1H NMR (300 MHz, $CDCl_3$): δ7.42 (1H, *s*, H-3), 5.59 (1H, *d*, J = 6 Hz, H-1), 5.27 (1H, *t*, J = 9 Hz, H-3′), 5.15 (1H, *m*, H-8), 5.13 (1H, *t*, J = 9 Hz, H-4′), 5.01 (1H, *dd*, J = 9 Hz, H-2′), 4.99 (1H, *d*, J = 6 Hz, H-1′), 4.31 (1H, *dd*, J = 4.5, 12 Hz, H-6a′), 4.16 (1H, *d*, J = 12 Hz, H-6b′), 3.77 (1H, *m*, H-5′), 3.70 (3H, *s*, OMe), 3.3 (1H, *m*, H-9), 2.64 (1H, *m*, H-6a), 2.42 (1H, *m*, H-6b), 2.1 (1H, *m*, H-5), 1.99–2.08 (15H, 5*s*, 5 × COMe), 1.32 (3H, *d*, J = 6 Hz, H-10).

This sample of diderroside tetra-acetate was treated with ethereal CH_2N_2 to give the methyl ester as a gum; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.41 (1H, *s*, H-3), 5.57 (1H, *d*, $J = 6$ Hz, H-1), 5.24 (1H, *t*, $J = 9$ Hz, H-3′), 5.12 (1H, *t*, $J = 9$ Hz, H-4′), 5.1 (1H, *m*, H-8), 5.03 (1H, *t*, $J = 9$ Hz, H-2′), 4.95 (1H, *d*, $J = 7.5$ Hz, H-1′), 4.28 (1H, *dd*, $J = 4.5, 12$ Hz, H-6a′), 4.14 (1H, *dd*, $J = 2, 12$ Hz, H-6b′), 3.72 (1H, *m*, H-5′), 3.67 (3H, *s*, OMe), 3.62 (3H, *s*, OMe), 3.26 (1H, *m*, H-5), 2.56 (1H, *dd*, $J = 6, 16.5$ Hz, H-6a), 2.49 (1H, *dd*, $J = 7.5, 16.5$ Hz, H-6b), 2.14, 2.06, 2.01, 1.98, (15H, 5*s*, 5 × COMe), 2.1 (1H, *m*, H-9), 1.31 (3H, *d*, $J = 6$ Hz, H-10). These assignments were confirmed by decoupling H-5′, H-5, H-9 and H-10. EIMS 70 eV, *m/z* (rel. int.): 587.1586 (0.1), calc. for $C_{26}H_{35}O_{15}$; 587.1583 $[M]^+$, 239.0913 (15.6), calc. for $C_{12}H_{15}O_5$; 239.0919 $[M - \text{glucose tetra-acetate} - MeCOOH]^+$, 165.0556 (73.0), calc. for $C_9H_9O_3$; 165.0554 [3-carbomethoxy-5-vinylpyrilium]$^+$, 139.0396 (26.4), calc. for $C_7H_7O_3$; 139.0395 [3-carbomethoxypyrilium]$^+$.

Comparison of methyl diderroside tetra-acetate with alpigenoside penta-acetate (300 MHz ^{1}H NMR, TLC) showed that the two were identical.

Acknowledgements—We thank Professor R. F. Raffauf for a sample of quinovic acid and Professor F. Bailleul for a sample of penta-acetyl alpigenoside. We are grateful to Dr. D. S. Leitch, Dr. P. G. Waterman and Dr. G. H. Dewar for assistance, and to Dr. S. R. Hemingway for her association with the work in the earlier stages.

REFERENCES

1. Henry, T. A. (1924) *Plant Alkaloids* p. 443. Churchill, London.
2. McLean, S. and Murray, D. G. (1970) *Can. J. Chem.* **48**, 867.
3. McLean, S. and Murray, D. G. (1972) *Can. J. Chem.* **50**, 1478.
4. Murray, D. G., Szakolcai, A. and McLean, S. (1972) *Can. J. Chem.* **50**, 1486.
5. Dmitrienko, G. I., Murray, D. G. and McLean, S. (1974) *Tetrahedron Letters* 1961.
6. Dmitrienko, G. I., Szakolcai, A. and McLean, S. (1974) *Tetrahedron Letters* 2599.
7. McLean, S. and Murray, D. G. (1972) *Can. J. Chem.* **50**, 1496.
8. Hemingway, S. R. and Phillipson, J. D. (1979) *Indole and Biogenetically Related Alkaloids* (Phillipson, J. D. and Zenk, M. H., eds.) p. 70. Academic Press, New York.
9. King, F. E. and Jurd, L. (1953) *J. Chem. Soc.* 1192.
10. Adeoye, A. O., Hemingway, S. R. and Waigh, R. D. (1981) *J. Pharm. Pharmacol.* **33**, 53P.
11. Sahu, N. P., Mahato, S. B., Banerji, N. and Chakravarti, R. N. (1974) *Indian J. Chem.* **12**, 284
12. Hui, W. H. and Li, M. M. (1975) *Phytochemistry* **15**, 985.
13. Tschesche, R., Duphorn, I. and Snatzke, G. (1963) *Justus Liebig's Ann. Chem.* **667**, 151.
14. El-Naggar, L. J. and Beal, J. L. (1980) *J. Nat. Prod.* **43**, 649.
15. Bock, K., Jensen, S. R. and Nielsen, B. J. (1976) *Acta Chem. Scand. Ser. B* **30**, 743.
16. Hostettman, K., Doumas, J. and Hardy, M. (1981) *Helv. Chim. Acta.* **64**, 297.
17. Inouye, H., Yoshida, T., Tobita, S., Tanaka, K. and Nishioka, T. (1974) *Tetrahedron* **30**, 201.
18. Bailleul, F., Leveau, A. M. and Durand, M. (1981) *J. Nat. Prod.* **44**, 573.
19. Raffauf, R. F., Le Quesne, P. W. and Ghosh, P. C. (1978), *J. Nat. Prod.* **41**, 432.
20. Fujita, E., Fujita, T. and Suzuki, T. (1967) *Chem. Pharm. Bull.* **15**, 1682.
21. Ferrari, F., Kiyan de Cornelio, I., Delle Monache, F. and Marini Bettolo, G. B. (1981) *Planta Med.* **43**, 24.