qualitativ durch DC am $AgNO_3$-imprägnierten Si gel getrennt. Da jedoch die Trennung sehr verlustreich ist, wurde auf eine präparative Trennung verzichtet.

Dec-1c-*en*- bzw. *Non*-1c-*en*-6.8-*diinsäure*-2-*phenylethyl*-*amid* (**3** *und* **4**). Farbloses Öl, IR cm^{-1}: 3450, 1690, 1500 (CONHR), 3310 (C≡CH), 2240 (C≡C), 1640 (C=C); MS: M^+ *m/e* 165.147 (18%) und 251.131 (17) ($C_{18}H_{19}NO$ bzw. $C_{17}H_{17}NO$); $-PhCH_2CH_2NH$ 145 (24) bzw. 131 (85); $PhCH_2CH_2$ 105 (60); $PhCH{=}CH_2^+$ 104 (100); $C_7H_7^+$ 91 (81).

Dec-1c-*en*- bzw. *Non*-1c-*en*-6.8-*diinsäure*-cis-*styrylamid* (**5** *und* **6**). Farbloses Öl, IR cm^{-1}: 3440, 1690, 1500 (CONHR), 3320 (C≡CH) m 2230 (C≡C), 1650 (C=C); MS: M^+ *m/e* 263.131 (8%) und 249.115 (30) ($C_{18}H_{17}NO$ bzw. $C_{17}H_{15}NO$); $-PhCH{=}CHNH$ 145 (28) bzw. 131 (80); $C_7H_7^+$ 91 (100).

Dec-1c-*en*- bzw. *Non*-1c-*en*-*säure*-trans-*styrylamid* (**7** *und* **8**). Farbloses Öl, IR cm^{-1}: 3440, 1695, 1510 (CONHR), 3320 (C≡CH), 2240 (C≡C), 1650 (C=C); MS: M^+ *m/e* 263.131 (6%) und 249.115 (17) ($C_{18}H_{17}NO$ bzw. $C_{17}H_{15}NO$); $-PhCH{=}CHNH$ 145 (45) bzw. 131 (35); $C_7H_7^+$ 91 (100).

1,2-*Epoxy*-*nona*-6.8-*diinsäure*-cis-*styrylamid* (**9**). Farbloses, nich völlig frei von **7** und **8** erhaltenes Öl, IR cm^{-1}: 3440, 1700, 1510 (CONHR), 3320 (C≡CH); MS: M^+ *m/e* 265.110 ($C_{17}H_{15}NO_2$).

Dodeca-2t.4t.8c.10t-*tetraensäureisobutylamid* (**10**). Farbloses Öl, IR cm^{-1}: 3460, 1690, 1510 (CONHR), 1640, 1620, 1005, 955 (C=CH); MS: 247.194 (4%) ($C_{16}H_{25}NO$); $-C_6H_8$ 167 (50); $C_6H_9^+$ 81 (100).

Danksagung—Der Deutschen Forschungsgemeinschaft daken wir für die Förderung dieser Arbeit.

LITERATUR

1. Stuessy, T. F. (1977) *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.) S. 622. Academic Press, London.
2. Seshadri, T. und Vedanthan, T. (1975) *Phytochemistry* **13**, 1666.
3. Bohlmann, F., Burkhardt, T. und Zdero, C. (1973) *Naturally Occurring Acetylenes*. Academic Press, London.
4. Jacobson, M. (1957) *Chem. Ind.* 50.
5. Bohlmann, F. und Zdero, C. (1973) *Chem. Ber.* **106**, 1328.

Phytochemistry, 1980, Vol. 19, pp. 1537–1539. Pergamon Press Ltd. Printed in England.

NEW S-PRENYL THIOESTERS FROM ESSENTIAL OILS OF SOME RUTACEAE

WILLIAM E. CAMPBELL,* GORDON M. L. CRAGG,* GORDON S. RITCHIE* and DOUGLAS E. A. RIVETT†

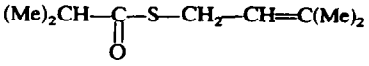
*Department of Organic Chemistry, University of Cape Town, Rondebosch 7700, South Africa; †Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

(*Revised received* 29 *October* 1979)

Key Word Index—*Phyllosma capensis*; *Agathosma apiculata*; *A. clavisepala*; *A. puberula*; Rutaceae; *S*-prenyl thioesters; *S*-(3-methyl-2-butenyl)-2-methylpropanethioate; *S*-(3-methyl-2-butenyl)-ethanethioate; *S*-(3-methyl-2-butenyl)-3-methyl butanethioate.

INTRODUCTION

The presence of sulphur-containing compounds in the essential oils of several Rutaceous taxa was first reported by van der Riet [1], Smith and Rivett [2] and Smith and Roux [3]. However, the structures proposed for these compounds, viz. butyl-1-pentenyl disulphide and bis-(2-pentenyl) tetrasulphide were never confirmed and in 1974 Rivett *et al.* [4, 5] isolated and identified *S*-(3-methyl-2-butenyl)-2-methylpropanethioate (**1**) as the major sulphur compound from the oils of *Agathosma apiculata*, *A. clavisepala* and *A. puberula*. This represented the first isolation of a naturally occurring *S*-prenyl thioester—other thioesters previously reported were those discovered by Moore and his associates in the seaweed genus *Dictyopteris* [6, 7] and by Burrell *et al.* in Galbanum oil [8]. Disulphides could also be detected in this essential oil but only under chromatographic conditions which suggested that these might be artefacts. The percentage of thioester (**1**) in each of the *Agathosma* oils did not account for the total sulphur content of the oils, indicating that other, as yet undetermined, sulphur compounds must also be present.

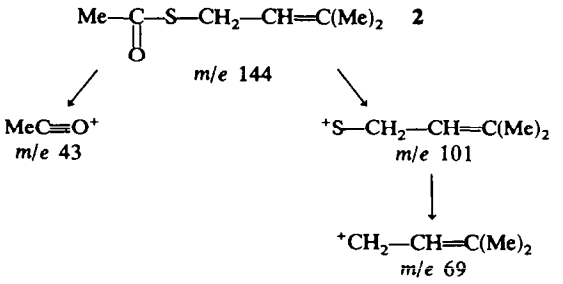


1

During the course of our studies on the isolation of alkaloids, coumarins and essential oils from the Rutaceae, we established the presence of sulphur in the oil from *Phyllosma capensis* Bolus. GLC and GC–MS analysis of the oil revealed the presence of 3 sulphur compounds. Their structures were established as **1** and two new *S*-prenyl thioesters, *S*-(3-methyl-2-butenyl)-ethanethioate (**2**) and *S*-(3-methyl-2-butenyl)-3-methyl butanethioate (**3**). The oils from *A. apiculata*, *A. clavisepala* and *A. puberula* were then re-examined by GC–MS and all three were shown to contain compound (**3**).

RESULTS AND DISCUSSION

Compound **2**, the second most abundant constituent of the oil from *P. capensis* was isolated by preparative GLC. The IR spectrum showed absorption at 1685 cm^{-1} (C=O) and 1622 cm^{-1} (C=C). The 100 MHz ^1H NMR spectrum clearly defined all 12 protons. The 6 proton-singlet at δ 1.7 was assigned to the $=C(Me)_2$ group. The presence of the MeCO group was evident from the 3 proton-singlet at δ 2.31. The 2 proton-doublet ($J = 8$ Hz) at 3.51 was assigned to CH_2 and the triplet ($J = 8$ Hz), with long range coupling to the $=C(Me)_2$ group ($J = 1.5$ Hz), at 5.2 was attributed to CH=. The MS gave a M^+ at *m/e* 144.0610 (calc. for $C_7H_{12}OS$ 144.0609) and fragment ions at 101.0429 (calc. for C_5H_9O 101.0425), 69.0707 (calc. for C_5H_9 69.0705) and 43.0154 (calc. for C_2H_3O 43.0184).



It was not possible to isolate thioester **3** by preparative GLC since it comprised only 3% of the oil and was part of a partially resolved double peak. The structure was thus initially assigned on the basis of accurate mass measurements. The M^+ occurred at *m/e* 186.1082 (calc. for $C_{10}H_{18}OS$ 186.1079), and the MS showed significant fragment ions at *m/e* 129.0370 (calc. for C_6H_9OS 129.0374), 101.0418 (calc. for C_5H_9S 101.0425), 85.0648 (calc. for C_5H_9O 85.0653), 69.0676 (calc. for C_5H_9 69.0704), 57.0715 (calc. for C_4H_9 57.0704) and 41.0366 (calc. for C_3H_5 41.0391).

The structures of **2** and **3** were confirmed by synthesis from 3-methylbut-2-enethiol and ethanoyl chloride and 3-methylbutanoyl chloride respectively. The IR, ^1H NMR and MS of synthetic **2** were identical to those of the fraction isolated from the oil. The synthetic thioester **3** gave IR absorption at 1680 (C=O) and 1625 cm^{-1} (C=C), and in the ^1H NMR spectrum, the doublet at δ 0.95 (6H, $J = 6$ Hz), the multiplet at 2.16 (1H, $J = 6.5$ Hz) and the doublet at 2.42 (2H, $J = 7$ Hz) were consistent with the 3-methylbutanoyl group. The MS of the synthetic and naturally occurring materials were identical.

The gas chromatogram of the volatile oil of *P. capensis* showed *ca* 25 peaks and some of the identified terpenoid components were (%): β-pinene (1.3); myrcene (0.7); camphene (1.1); limonene (1.3); linalyl acetate (6.9); β-phellandrene (5.1); ocimene (5.3); terpinen-4-ol (13.5) and α-terpineol (3.2), together with the three sulphur compounds, **1** (6.3), **2** (9.6) and **3** (3.0).

EXPERIMENTAL

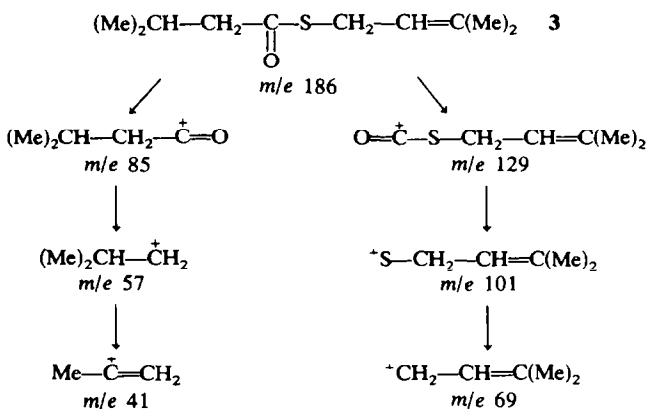
P. capensis Bolus was collected in the Wupperthal district of the Cape Province. (Representative voucher specimen Williams 2125 in the Compton Herbarium, Kirstenbosch National Botanical Gardens, Cape Town.)

^1H NMR spectra were recorded in $CDCl_3$ at 100 MHz using TMS as int. standard. Optical rotation was measured in $CHCl_3$ and the refractive index on an Abbe refractometer. Prep.-GLC: 15% FFAP on Chromosorb W, 4 mm × 4 m glass column, temp. 150°, N_2 at 30 ml/min. GC–MS: FFAP 0.3 mm × 30 m SCOT stainless steel column, 1 μl, programmed 50–180° at 2°/min, He at 6 ml/min. MS were recorded at 70 eV.

Isolation of essential oil. Fresh stems, twigs and leaves (0.8 kg) were steam-distilled for 4 hr and the aq. distillate extracted twice with 300 ml $CHCl_3$. The $CHCl_3$ soln, dried (Na_2SO_4), was evapd *in vacuo* to give the oil (1.7 g, 0.21%). %S, 3.4, $[\alpha]_D^{20} + 1.49°$ ($CHCl_3$, *c* 1.05), N_D^{20} 1.4729.

S-(3-Methyl-2-butenyl)-ethanethioate (**2**) Ten 30 μl injections of the oil on to the prep. GLC column gave 25 mg **2**. (Found: S, 21.8 $C_7H_{12}OS$ requires: S, 22.2); IR ν_{max} cm^{-1}: 1622 (C=C), 1685 (C=O); ^1H NMR δ 1.7 (6H, *s*), 2.31 (3H, *s*), 3.51 (2H, *d*, $J = 8$ Hz), 5.2 (1H, *t*, $J = 8$ Hz, $J = 1.5$ Hz). MS: M^+ *m/e* 144.0610 (21%) (calc. for $C_7H_{12}OS$ 144.0609), 101.0429 (29%) (calc. for C_5H_9S 101.0425), 69.0707 (100%) (calc. for C_5H_9 69.0705), 43.0154 (4%) (calc. for C_2H_3O 43.0184).

Synthesis of **2**. 3-Methylbut-2-enethiol (2.5 ml), prepared from 1-chloro-3-methylbut-2-ene and thiourea [9] was dissolved in ice-cold dry Py (15 ml) and MeCOCl (4 ml) was added slowly with stirring. The mixture was warmed to room temp. and the soln extracted with Et_2O. The Et_2O soln was washed successively with dil solns of HCl and Na_2CO_3, dried and distilled to afford **2** (1 g), bp 70–72°/2 mm Hg. (Found: S,



22.1. Calc. for $C_7H_{12}OS$: S, 22,2); IR ν_{max} cm^{-1}: 1684 (C=O), 1624 (C=C); ^1H NMR: δ 1.68 (6H, *s*), 2.28 (3H, *s*), 3.5 (2H, *d*, $J = 8$ Hz), 5.19 (1H, *t*, $J = 8$ Hz, $J = 1.5$ Hz). MS: M^+ *m/e* 144.0610 (16%) (calc. for $C_7H_{12}OS$ 144.0609), 101.0418 (30%) (calc. for C_5H_9S 101.0425), 69.0716 (100%) (calc. for C_5H_9 69.0705), 43.0152 (3%) (calc. for C_2H_3O 43.0184).

S-(3-Methyl-2-butenyl)-3-methyl butanethioate **3**. MS: M^+ *m/e* 186.1082 (8%) (calc. for $C_{10}H_{18}OS$ 186.1079), 129.0370 (4%) (calc. for C_6H_9OS 129.0374), 101.0418 (8%) (calc. for C_5H_9S 101.0425), 85.0648 (69%) (calc. for C_5H_9O 85.0653), 69.0676 (80%) (calc. for C_5H_9 69.0704), 57.0715 (100%) (calc. for C_4H_9 57.0704), 41.0366 (70%) (calc. for C_3H_5 41.0391).

Synthesis of **3**. 3-Methylbut-2-enethiol (2.5 ml) in Py (15 ml) was reacted with 3-methylbutanoyl chloride (6 ml) as described above to give 1.7 g **3**, bp 88–92°/4 mm Hg. (Found: S, 16.9. Calc. for $C_{10}H_{18}OS$: S, 17.2); IR ν_{max} cm^{-1}: 1682 (C=O), 1627 (C=C); ^1H NMR: δ 0.95 (6H, *d*, $J = 6$ Hz), 1.7 (6H, *s*), 2.16 (1H, *m*, $J = 6$ Hz), 2.42 (2H, *d*, $J = 7$ Hz), 3.53 (2H, *d*, $J = 7$ Hz), 5.22 (1H, *t*, $J = 7$ Hz, $J = 1.5$ Hz). MS: M^+ *m/e* 186.1084 (19%) (calc. for $C_{10}H_{18}OS$ 186.1079), 129.0369 (1%) (calc. for C_6H_9OS 129.0374), 101.0416 (11%) (calc.. for C_5H_9S) 101.0425), 85.0636 (79%) (calc. for C_5H_9O 85.0653), 69.0672 (95%) (calc. for C_5H_9 69.0704), 57.0748 (100%) (calc. for C_4H_9 57.0704), 41.0417 (74%) (calc. for C_3H_5 41.0391).

S-(3-Methyl-2-butenyl)-2-methyl propanethioate (**1**). MS: M^+ *m/e* 172.0921 (19%) (calc. for $C_9H_{16}OS$ 172.0922), 129.0374 (11%) (calc. for C_6H_9OS 129.0374), 101.0417 (18%) (calc. for C_5H_9S 101.0425), 71.0457 (85%) (calc. for C_4H_7O 71.0497), 69.0678 (100%) (calc. for C_5H_9 69.0704).

Acknowledgements—Financial assistance from the University of Cape Town is gratefully acknowledged. We thank Mr. W. R. T. Hemsted for the sulphur analyses, Mrs. A. Bean for the collection and authentication of the plant material, and the University of Stellenbosch for recording the high resolution MS.

REFERENCES

1. van der Riet, B. de St. J. (1933) *Proc. Chem. Met. Mining Soc. S. Afr.* **34**, 80.
2. Smith, J. L. B. and Rivett, D. E. A. (1946) *Trans. R. Soc., S. Afr.* **31**, 111.
3. Smith, J. L. B. and Roux, D. G. (1947) *Trans. R. Soc., S. Afr.* **31**, 333.
4. Rivett, D. E. A. (1974) *Tetrahedron Letters* 1253.
5. Moran, V. C., Persicaner, P. H. R. and Rivett, D. E. A. (1975) *J. S. Afr. Chem. Inst.* **28**, 47.
6. Roller, P., Au, K. and Moore, R. E. (1971) *Chem. Commun.* 503.
7. Moore, R. E., Mistysyn, J. and Pettus, J. A. (1972) *Chem. Commun.* 326.
8. Burrell, J. W. K., Lucas, R. A., Michalkiewicz, D. M. and Riezebos, G. (1971) *Tetrahedron Letters* 2837.
9. Urquhart, G. C., Gates, J. W. and Connor, R. (1941) *Org. Synth.* **21**, 36.

Phytochemistry, 1980, Vol. 19, pp. 1539–1541. Pergamon Press Ltd. Printed in England.

PANAXYDOL, A NEW POLYACETYLENIC EPOXIDE FROM *PANAX GINSENG* ROOTS

JANUSZ POPŁAWSKI, JERZY T. WROBEL and TOMASZ GLINKA

Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

(*Received* 8 *October* 1979)

Key Word Index—*Panax ginseng*; Araliaceae; polyacetylenic alcohol; 9,10-epoxy-3-hydroxyheptadeca-1-en-4,6-diyne; synthesis.

A new polyacetylenic compound named panaxydol was isolated from *Panax ginseng* C. A. Meyer roots together with falcarinol, 3-hydroxyheptadeca-1,9c-dien-4,6-diyne (**1**), previously described by Bohlmann [1, 2], Takahashi [3] and Jones [4]. Spectroscopic data showed the compound to be a derivative of a polyacetylenic alcohol with a structure similar to **1**.

The existence in **1** of a terminal olefinic bond and of unsaturation equivalent to 5 mol of hydrogen was demonstrated by ozonolysis and catalytic hydrogenation. Bands at 2270 and 1650 cm^{-1} in the IR spectrum indicated the presence of acetylenic and olefinic bonds. The chemical shifts and coupling constants of three of the protons were identical to those of the terminal structure of falcarinol (Scheme 1).

Since no other olefinic or acetylenic protons were observed in the ^1H NMR spectrum, the remaining multiple bonds were assigned to two conjugated acetylenic bonds. The IR band at 2270 cm^{-1} is characteristic of conjugated diacetylenes directly bonded to the —CHOH group [5]. Analysis of the ^1H NMR spectrum, together with the conversion of panaxydol