less compounds, phytanyl-glycerol diether, geranylgeraniol and phytanol, have now been isolated and identified. The phytanyl-glycerol diether was obtained as a colourless viscous oil with optical rotations ranging between $[\alpha]_D$ + 8.5–9.0 ($CHCl_3$; *c*, 2.6). The dextrorotatory nature of the compound indicated that the diether has *sn*-2,3-structure and configuration because synthetic *sn*-1,2-dialkyl glycerol ethers are laevorotatory [2]. The IR and NMR spectra were identical to those of a synthetic sample [2–4]. Geranylgeraniol was also obtained as a colourless oil and its IR, NMR spectra and GLC retention time (10% SP-2300) were identical with an authentic sample [3]. The identity and the amount of phytanol were determined by GLC.

The wide occurrence of large amounts of free phytanylglycerol diether in several strains of extreme halophilic bacteria is highly significant, since it is the common backbone of all the phospho- and glycolipids in these organisms. It would thus appear that phytanylglycerol diether plays a key role in the biosynthesis of phospho- and glycolipids, although the biosynthetic pathway of the phytanylglycerol diether moiety and diether lipids is still a mystery. Presumably, geranylgeraniol and phytanol play a key role in the biosynthesis of the diether moiety, probably via their pyrophosphates. Work on the biosynthesis of the diether lipids is in progress.

EXPERIMENTAL

Culture methods, harvesting of cells, lipid extraction procedures and separation of total lipids into polar and neutral lipids fractions are described elsewhere [3]. Neutral lipids were fractionated on a 3% H_2O (v/w) deactivated column of Al_2O_3 (18 × 3 cm) with C_6H_6 (600 ml, Fr. I), 1% Me_2CO in C_6H_6 (300 ml, Fr. II), 5% Me_2CO in C_6H_6 (300 ml, Fr. III), 10% Me_2CO in C_6H_6 (500 ml, Fr. IV) and pure MeOH (500 ml, Fr. V). Phytanylglycerol diether was purified from fraction III by TLC on Si gel H in $CHCl_3$–Et_2O (99:1, R_f 0.40) and on Al_2O_3 in $CHCl_3$–Et_2O (99.5:0.5, R_f 0.72). Geranylgeraniol was purified from fraction IV by TLC on Al_2O_3 in $CHCl_3$–Et_2O (99.5:0.5, R_f 0.46). The spots were detected by I_2 vapour. Phytanol was determined by applying column fraction IV to GLC on a 10% SP-2300 column (column temp.—180°, N_2 1 kg/cm^2, H_2 0.7 kg/cm^2, injector temp.—200°, detector temp.—230°). The relative retentions of phytanol, phytol and geranylgerniol were 2.08, 2.80 and 6.18, respectively (relative to methylpalmitate).

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REFERENCES

1. Kushwaha, S. C., Gochnauer, M. B., Kushner, D. J. and Kates, M. (1974) *Can. J. Microbiol* **20**, 241.
2. Kates, M. (1972) in *Ether Lipids* (Snyder, F., ed.) pp. 351–398. Academic Press, New York.
3. Kushwaha, S. C., Kramer, J. K. G. and Kates, M. (1975) *Biochim. Biophys. Acta* **398**, 303.
4. Joo, C. N., Shier, T. and Kates, M. (1968) *J. Lipid Res.* **9**, 782.

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IVALIN IN *GEIGERIA ASPERA*

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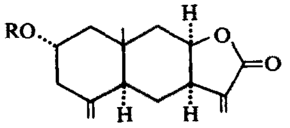
Key Word Index—*Geigeria aspera*; Compositae; eudesmanolide; ivalin; geigerinin; dihydrogriesenin.

Geigeria species, commonly known as the 'vomiting bush', are responsible for vomiting disease [1]. Several crystalline sesquiterpenoid lactones have been isolated from *G. aspera* Harv. and *G. filifolia* Mattf. From *G. aspera* were isolated geigerin [2, 3], vermeerin [4–6], geigerinin [7, 8] and dihydrogriesenin [9], while *G. filifolia* yielded gafrinin [10, 11], griesenin and dihydrogriesenin [12, 13]. Reinvestigation of *G. aspera* has resulted in the identification of ivalin (1). Dihydrogriesenin and geigerinin were also isolated.

Ivalin(1) has previously been isolated as the main sesquiterpene lactone from *Iva microcephala* Nutt. and *Iva imbricata* [14], collected in the Southern Coastal Plain of the USA. It was also shown to be present in *Zaluzania triloba* Pers [15] and *Polymnia leavigata* Beadle [16]. The structure of ivalin(1), the first eudesmanolide isolated from *Geigeria* species, was identified and confirmed by mp, PMR, IR, MS, accurate mass determination and rotation. The X-ray crystallography, by another group [17], on the bromoacetate(2) was in agreement with the known structure. Ivalin(1) as well as the known guaianolides from *Geigeria* species were toxic



(1) R = –H
(2) R = $-OCOCH_2Br$

to guinea-pigs [18]. The presence of ivalin(**1**) in *Geigeria* of the tribe Inuleae and in *Iva*, *Polymnia* and *Zaluzania* of the Heliantheae is of taxonomic interest.

EXPERIMENTAL

Geigeria aspera Harv. was collected through the courtesy of Dr T. W. Naude of the Onderstepoort Veterinary Research Institute, during March 1974 in the Ermelo district, Republic of South Africa. The plant was identified through the courtesy of the Director, Botanical Research Institute, Pretoria. Above-ground air-dried plant material (3 kg) was shaken twice with 96% EtOH for 24 hr. The combined extracts were dissolved in H_2O–EtOH (2:1,3 l.). The aq. soln was extracted with hexane (2 × 250 ml). The aq. phase, after removal of tar, was extracted with $CHCl_3$ (3 × 300 ml) which gave on evapn an oil (70 g). This oil was chromatographed in 2 26 g portions on Si gel (Merck Si gel 60, 800 g. 8 × 45 cm). The chromatography was controlled by TLC (Si gel, 4% MeOH–$CHCl_3$), C_6H_6–$CHCl_3$ (1:1), $CHCl_3$ and EtOH eluted fractions with mass 10.6, 4.6 and 9 g, respectively. Dihydrogriesenin (6 g) and geigerinin (1.1 g) were obtained by methods previously described [7, 9] from the C_6H_6–$CHCl_3$ and EtOH extracts, respectively. Rechromatography of the $CHCl_3$ extract on Si gel (100 g) eluted with $CHCl_3$ a fraction (2 g) which showed only 1 dark red spot on TLC when sprayed with 65% H_2SO_4. Several recrystallizations from MeOH gave 1.3 g (0.12%) ivalin (**1**), mp 131°.

Synthesis of the bromoacetate (**2**). To 410 mg of **1**, and Py (430 mg) in C_6H_6 (10 ml) cooled in ice, was added bromoacetyl bromide (930 mg). TLC indicated that the reaction was completed after 1 hr, when the reaction mixture was added to cold H_2O. C_6H_6 extraction and recrystallization from MeOH (twice) and Me_2CO gave 220 mg (36%) (**2**). Mp 207–210°. (Found: C, 55.30; H, 5.73; Br, 21.73. $C_{17}H_{21}O_4$ Br requires: C, 55.48; H, 5.92; Br, 21.73%). UV (c1.09 × 10^{-4} M, MeOH) ε_{210} 9374; ε_{250} 230. PMR (100 MHz, $CDCl_3$): δ 0.91 (*s*, 3H, —CH_3), 1.20–2.42 (*m*, 8H, —CH_2—), 2.79 (*ddd*, 1H, H-5), 2.80–3.16 (*m*, 1H, H-7), 3.79 (*s*, 2H, —CH_2Br), 4.52 (*dt*, 1H, H-8), 4.66 (*m*, 1H, $W_{\frac{1}{2}}$ = 4 Hz, H-14a), 4.98 (*br. s*, 1H, H-14b), 4.81–5.15 (*m*, 1H, H-2), 5.61 (*d*, 1H, H-13a) and 6.16 (*d*, 1H, H-13b). MS Abundant peaks EI: 230, 124, 119, 111, 97, 85, 83, 71 and 57. CI (isobutane) 371, 369, 131, 113 and 85.

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REFERENCES

1. Grosskopf, J. F. W. (1965) Tech. Comm. No. 21, Dept., Agric. Techn. Services Rep. of South Africa.
2. Rimington, C. and Roets, G. C. S. (1936) *Onderstepoort J. Vet. Sci.* 7, 485.
3. Hamilton, J. A., McPhail, A. T. and Sim, G. A. (1962) *J. Chem. Soc.*, 708.
4. Rimington, C., Roets, G. C. S. and Steyn, D. G. (1936) *Onderstepoort J. Vet. Sci.* 7, 507.
5. Anderson, L. A. P., De Kock, W. T., Pachler, K. G. R. and Brink, C. v.d. M. (1967) *Tetrahedron* **23**, 4153.
6. Hertz, W., Aota, K., Holub, M. and Samek, Z. (1970) *J. Org. Chem.* **35**, 2611.
7. De Villiers, J. P. (1959) *J. Chem. Soc.*, 2412.
8. De Villiers, J. P. (1963) *J. Chem. Soc.*, 4989.
9. Vermeulen, N. M. J., Vogelzang, M. E. and Potgieter, D. J. J. (1977) *Agrochemphysica* **10**, 1.
10. De Villiers, J. P. (1959) *S. Afr. Ind. Chem.* **13**, 194.
11. Anderson, L. A. P., De Kock, W. T., Nel, W., Pachler, K. G. R. and Van Tonder, G. (1968) *Tetrahedron* **24**, 1687.
12. De Kock, W. T., Pachler, K. G. R., Ross, W. F., Wessels, P. L. and Du Preez, I. C. (1968) *Tetrahedron* **24**, 6037.
13. De Kock, W. T., Pachler, K. G. R. and Wessels, P. L. (1968) *Tetrahedron* **24**, 6045.
14. Herz, W. and Högenhauer, G. (1962) *J. Org. Chem.* **27**, 905.
15. Romo De Vivar, A., Cabrera, A., Ortega, A. and Romo, J. (1967) *Tetrahedron* **23**, 3903.
16. Herz, W. and Bhat, S. V. (1970) *J. Org. Chem.* **35**, 2605.
17. Coetzer, J. and Kruger, G. J. *Acta Crystallogr.* (*in* press).
18. Vermeulen, N. M. J., Von Jeney De Borosjenö, N. L. T. R. M., Potgieter, D. J. J., Naude, T. W. and Kellerman, S. J. *Onderstepoort J. Vet. Sci.* (in press).