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REFERENCES

1. Bohlmann, F. and Grenz, M. (1979) *Phytochemistry* **18,** 491.
2. Bohlmann, F. and Knoll, K.-H. (1978) *Phytochemistry* **17,** 461.
3. Moriyama, Y., Tsuyuki, T., Takahashi, T. and Koyama, A. (1974) *Phytochemistry* **13,** 288.
4. Bohlmann, F., Ehlers, D., Zdero, C. and Grenz, M. (1977) *Chem. Ber.* **110,** 2640.
5. Bohlmann, F., Zdero, C. and Grenz, M. (1974) *Chem. Ber.* **107,** 3928.
6. Naves, Y. R. (1966) *Helv. Chim. Acta.* **49,** 1029.
7. Bohlmann, F., Dutta, L., Robinson, H. and King, R. M. (1979) *Phytochemistry* **18,** 1889.
8. Yoshihara, K., Ohta, Y., Sakai, T. and Hirose, Y. (1969) *Tetrahedron Letters* 2263.

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THE STRUCTURE AND STEREOCHEMISTRY OF SPERGULAGENOL, A TRITERPENE FROM *MOLLUGO SPERGULA*

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Key Word Index—*Mollugo spergula*; Ficoidaceae; triterpene; (21α-H)-hopane; spergulagenol.

INTRODUCTION

The isolation of two new triterpenes, spergulagenic acid [1–3] and spergulagenin-A [4–11], has been reported earlier from this laboratory. Another new triterpenoid sapogenin called spergulagenin-C (**1**), $C_{30}H_{50}O_5$, mp 274–278° (decomp.), has also been isolated and it has been shown to be x-hydroxy spergulagenin-A [12]. Kitagawa *et al.* [13] reported a new sapogenin, spergulatriol, from the same source. The present paper reports the structure of a new triterpene, called spergulagenol (**2a**), from the ethanolic extract of the same plant.

RESULTS AND DISCUSSION

Spergulagenol (**2a**), $C_{30}H_{52}O_4$, mp 295–298°, $[\alpha]_D$ + 46° (Py) gave a violet colour with the Liebermann–Burchard reagent but no colour with tetranitromethane. Its IR spectrum showed bands at 3320 and 3440 cm^{-1} for hydroxyl groups. Its MS showed the molecular ion peak at *m/e* 476 and a peak at *m/e* 59 due to the ion $(Me)_2C{=}\overset{+}{O}H$ formed by the cleavage of the hydroxy isopropyl sidechain (cf. mollugogenol-A [14, 15]). It also showed peaks at *m/e* 458 and 400 for the ion species **a** and **b** respectively.

Compound **2a** on treatment with acetic anhydride and pyridine at 0° yielded a triacetate (**2b**), $C_{36}H_{58}O_7$, mp 230–232°. Its MS did not show the molecular ion peak but showed a peak at *m/e* 584 for the $(M-H_2O)^+$ ion. Its ^1H NMR spectrum ($CDCl_3$, 90 MHz) showed singlets at δ0.87 (9H), 0.90 (3H), 1.03 (3H), 1.15 (3H) and 1.19 (6H) for the eight quarternary methyl groups (—$\overset{|}{\underset{|}{C}}$—$\underline{CH_3}$). The singlets at δ2.02 (3H), 2.03 (3H) and 2.07 (3H) were attributed to the three acetoxy groups (—O—CO—$\underline{CH_3}$). The broad signals centred at 4.49 (1H, *m*), 5.25 (1H, *m*) and 4.88 (1H, *m*) were assigned to 3-αH, 12-αH and 16-αH, respectively. The signal for the 22-OH group appeared at 3.5 and disappeared on D_2O exchange.

Oxidation of **2a** with CrO_3 in acetic acid at room temp. yielded a monohydroxy triketone (**3**), $C_{30}H_{46}O_4$, mp 254–256°. Its IR spectrum (in Nujol mull) showed bands at 3350 (OH) and 1695–1700 cm^{-1} (six-membered ring ketone). It gave a positive Zimmerman colour reaction (3-keto group) and did not respond to the ferric chloride colour test. Its MS did not show the molecular ion peak at *m/e* 470 but showed a strong peak at 452 $(M-H_2O)^+$. The MS fragmentation pattern was very characteristic of 12-keto compounds (cf. spergulagenin-A [4–11]). There was a peak at *m/e* 247, for the ion species **c** and at *m/e* 219 arising out of

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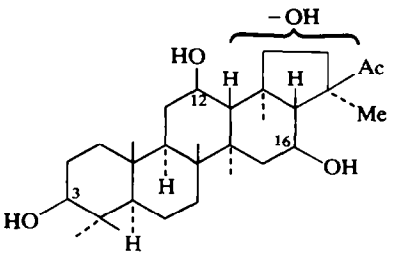

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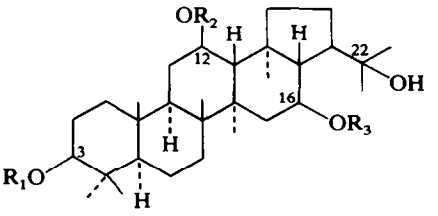
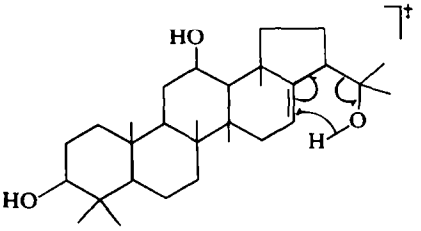
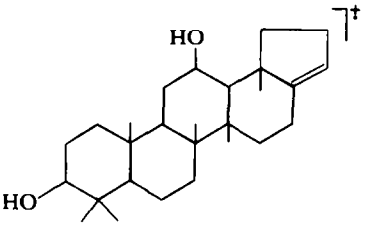


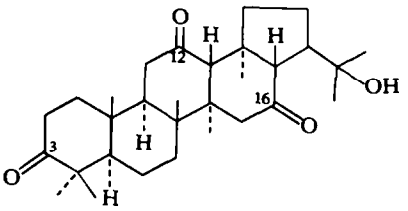
2a $R_1 = R_2 = R_3 = H$
2b $R_1 = R_2 = R_3 = Ac$



a *m/e* 458



b *m/e* 400



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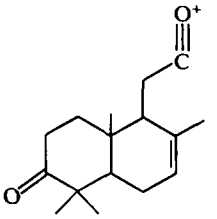
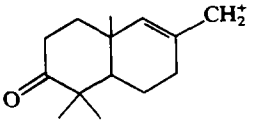


c *m/e* 247



d *m/e* 205

loss of 28 mu (CO) from ion species **c**. There was also a peak at *m/e* 205 for ion **d** arising by the usual cleavage through ring C.

Hopane and (21α-H)-hopane derivatives having hydroxyl groups at C-22 and C-16 give hop-15,17(21)-dienes on treatment with ethanolic hydrogen chloride [14–16]. Under similar conditions spergulagenol yielded a diene, not isolated in pure state, which showed UV absorption maxima at 243, 251 and 261 nm characteristic of hop-15,17(21)-dienes. This indicated the presence of a secondary hydroxyl group at C-16 and a tertiary hydroxyl group at C-22. Spergulagenol, unlike 22-hydroxy-hopane derivatives [17], did not undergo hydrogenolysis in the presence of Adam's platinum catalyst, and this indicated the probability of spergulagenol being a 22-hydroxy(21α-H) hopane derivative.

The monohydroxy triketone (**3**) on Huang Minlon reduction furnished a compound, mp 225–227°, $C_{30}H_{52}O$, which was characterized as 22-hydroxy-(21α-H)-hopane by direct comparison of mp, TLC and IR spectrum with an authentic sample.

On the basis of the data presented above spergulagenol is considered to be 3,12,16,22-tetrahydroxy-(21α-H)-hopane. Spergulagenol formed the triacetate (**2b**) on treatment with acetic anhydride and pyridine at 0°. The ease of acetylation indicated the equatorial orientation of the secondary hydroxyl groups and hence the structure and stereochemistry of spergulagenol is represented as **2a**.

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REFERENCES

1. Chakrabarti, P., Mukherjee, D. K. and Barua, A. K. (1966) *Tetrahedron* **22**, 1431.
2. Chakrabarti, P., Mukherjee, D. K., Barua, A. K. and Das, B. C. (1968) *Tetrahedron* **24**, 1107.
3. Chakrabarti, P. and Barua, A. K. (1969) *J. Indian Chem. Soc.* **46**, 626.
4. Chakrabarti, P. and Barua, A. K. (1965) *J. Indian Chem. Soc.* **42**, 137.

5. Chakrabarti, P. (1967) *J. Indian Chem. Soc.* **44,** 242.
6. Chakrabarti, P., Basak, A. and Barua, A. K. (1972–1974) Annu. Report, Bose Institute, p. 15.
7. Basak, A. (1974) Part of the Ph.D. (Sc.) thesis submitted to the Calcutta University.
8. Kitagawa, I., Suzuki, H. and Yosioka, I. (1974) *Tetrahedron Letters* 1173.
9. Kitagawa, I., Suzuki, H., Kitazawa, K., Yamo, N. and Yosioka, I. (1975) *Chem. Pharm. Bull.* **23,** 355.
10. Chakrabarti, P., Basak, A. and Barua, A. K. (1977) *Trans. Bose Res. Inst.* **40,** 117.
11. Barua, A. K., Basak, A., Banerjee, S. K., Chatterjee, T., Basu, K. and Chakrabarti, P. (1978) *Trans Bose Res. Inst.* **41,** 83.
12. Barua, A. K., Banerjee, S. K., Das Gupta, C., Basak, A. and Chakrabarti, P. (1977) 64th Session of the Indian Sci. Congr. Abstracts. Bhubaneswar, January 1977, Org. 18.
13. Kitagawa, I., Yamanaka, H., Nakanishi, T. and Yosioka, I. (1976) *Tetrahedron Letters* 2327.
14. Chakrabarti, P. (1969) *J. Indian Chem. Soc.* **46,** 98.
15. Chakrabarti, P. (1969) *Tetrahedron* **25,** 3301.
16. Yosioka, I. and Nakanishi, T. (1963) *Chem. Pharm. Bull.* **11,** 1468.
17. Corbett, R. E. and Smith, R. A. J. (1967) *J. Chem. Soc.* 1622.

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A NEW TRITERPENOID GLYCOSIDE FROM THE SEEDS OF *GLINUS LOTOIDES*

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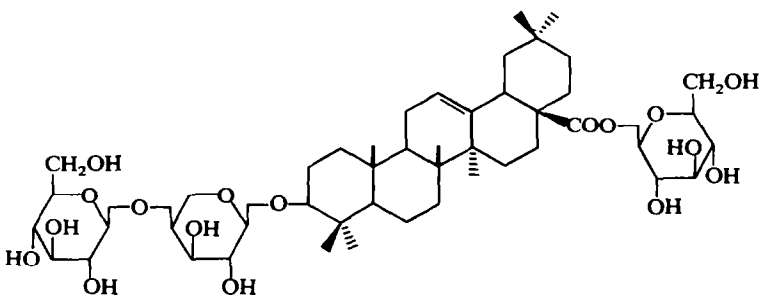
Key Word Index—*Glinus lotoides*; Aizoaceae; triterpene glycoside; oleanolic acid; anthelmintic.

It was reported recently that the anthelmintic property of the seeds of *Glinus lotoides* is due to saponins [1, 2]. The isolation of several sapogenins and a saponin from *Mollugo hirta* (which is synonymous with *G. lotoides*) has also been reported [3]. In this communication we report on the structure of a new triterpene glycoside isolated from the seeds.

The powdered seeds (100 g) were defatted and extracted with 80% aqueous ethanol. Addition of diethylether gave a precipitate (6 g) which was acetylated with acetic anhydride and pyridine. The crude acetylated product (5 g) was chromatographed using 300 g Si gel 60 and eluted with chloroform containing increasing amounts of ethyl acetate (300 ml fractions). Fractions 32–46 (eluted with 30% ethyl acetate) gave 2.0 g of a compound which was homogeneous on TLC. Repeated recrystallization from methanol gave a crystalline substance $C_{67}H_{96}O_{27}$, mp. 186–189°, $[\alpha]_D^{21}$ + 37° (MeOH; *c* 1.5). Deacetylation with methanolic ammonia [4] gave a biologically active saponin (**1**) which could be reacetylated to the same compound obtained from the column.

Deacetylation gave a saponin, which upon recrystallization from methanol gave plates $C_{47}H_{76}O_{17}$, mp 255° (dec.), $[\alpha]_D^{21}$ + 20° (MeOH; *c* 0.8). Acid hydrolysis of the saponin with 8% methanolic HCl yielded oleanolic acid, D-glucose and L-arabinose. The glucose–arabinose ratio was found to be 2:1 by GLC



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