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TRITERPENES OF *SARCOSTEMMA* ASCLEPIADACEAE

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Key Word Index—*Sarcostemma* sp.; Asclepiadaceae; triterpenes; germanicol butyrate.

Abstract—A mixture of *n*-alkanes, four pentacyclic triterpenes, and the butyrate of germanicol were isolated and their structures established.

INTRODUCTION

Sarcostemma sp. is a creeper found in the semi-arid region of Lagunillas, State of Mérida, Venezuela. From the stems and leaves of this plant, we have isolated a mixture of aliphatic hydrocarbons, germanicol acetate, germanicol butyrate, lupeol, taraxerol, and germanicol. We wish to present the experimental details of this work.

RESULTS AND DISCUSSION

Column chromatography of the concentrated benzene extract over silica yielded initially a wax which was shown by MS and IR to be probably a mixture of C_{29}, C_{31}, C_{33} η-alkanes. The mass spectrum of this wax shows the three molecular ion peaks at *m/e* 408, 436 and 464 along with a gradual increase in the abundance of the C_nH_{2n+1} fragments suggesting that the compounds are saturated, straight chain hydrocarbons [1, 2]. This mixture of aliphatic hydrocarbons has recently been isolated from *Zataria multiflora* [3], *Schkuhria pinnata* [4], *Catharanthus longifolius* [5] and *Artirrhinum majus* [6].

Continued elution of the column yielded a mixture of four components (TLC) that was impossible to resolve by conventional column chromatography, but a partial separation was obtained by using high pressure liquid chromatography (HPLC). Further elution afforded lupeol, taraxerol and germanicol identical (TLC, IR, m.p., MS, acetates) with authentic samples.

The HPLC separation afforded two pure compounds whose IR spectra exhibited a carbonyl peak in the 1725 cm^{-1} region and C–O–C stretching band in the 1255 cm^{-1} region, indicative of an ester function. Hydrolysis of both these esters with 15% KOH in EtOH–ØH–H_2O (80:10:10) yielded a triterpene which was identified as germanicol (IR, NMR, m.p.) [7, 8]. The more polar ester was shown to be identical (IR, NMR, MS, m.p.) with an authentic sample of germanicol acetate. The less polar ester was identified as the butyrate of germanicol. The NMR of the butyrate shows the expected distorted triplete at 2·23 δ, while the MS shows an M-88 ion as well as the fragments characteristic of a Δ^{18}-oleanene derivative [9].

EXPERIMENTAL

A voucher specimen No. MFK 28 has been deposited in the herbarium of the Dept. de Botánica, Universidad de Los Andes. MS were recorded at 70 eV; NMR spectra were recorded in $CDCl_3$ solutions with TMS as an internal standard; High pressure column chromatography was carried out on silica gel H(Merck) and using a Chromatronix column (2·5 × 40 cm) and pump. Extraction of *Sarcostemma* sp. The air-dried and ground plant (400 g) was extracted with benzene (5 l) at room temp for 4 days. Concentration of the extract yielded a dark green oil which was separated on a column of silica with increasing conc of C_6H_6 in light petrol. (0:100 to 50:50).

Germanicol butyrate, m.p. 238–239°, acetone or di-isopropyl ether/MeOH. ν_{max} (KBr): 2948, 1726, 1643, 1380, 1361, 1263, 1187, 1095, 1033, 987, 851, 803 cm^{-1}. NMRδ: ($CDCl_3$) 0·72 (*s*, 3H), 0·83 (*s*, 6H), 0·89 (*s*, 3H), 0·93 (*s*, 6H), 1·00 (*s*, 3H), 1·05 (*s*, 3H), 2·23 (*t*, J = 7Hz, $MeCH_2CH_2COO$–), 4·44 (*m*, H at C-3), 4·80 (*s*, H at C-19). MS: *m/e*(%) 496(1·2), 481(2·4), 467(0·3), 408(3·7), 393(5·5), 277(0·7), 218(10·6), 205(34), 204(84), 203(18·8), 191(16·4), 190(24·6), 189(100), 178(13·5), 177(79·7), 176(13·5), 175(25·6), 161(21·3).

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REFERENCES

1. Budzikiewicz, H., Djerassi, C. and Williams, D. (1967) *Mass Spectrometry of Organic Compounds*, p. 50, Holden-Day, San Francisco.
2. Biemann, K. (1962) *Mass Spectrometry*, p. 78, McGraw-Hill, New York.
3. Gupta, G. and Gupta, N. L. (1972) *Phytochemistry* **11**, 455.
4. Flematti, S. and Gros, E. (1971) *An. Asoc. Quim. Argent.* **59**, 405.
5. Farnsworth, N. and Hoerhammer, H. P. (1968) *Phytochemistry* **7**, 887.
6. Guelz, P. (1968) *Phytochemistry* **7**, 1009.
7. Ireland, R. and Johnson, W. (1970) *J. Am. Chem. Soc.* **92**, 5743.
8. Radt, F. (ed.), *Elsevier's Encyclopedia of Organic Chemistry* **14**, p. 1065s, Elsevier, New York (1952).
9. Budzikiewicz, H., Wilson, J. and Djerassi, C. (1963) *J. Am. Chem. Soc.* **85**, 3688.

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PILOCEREINE FROM *LOPHOCEREUS SCHOTTII* FORMAE *MONSTROSUS* AND *MIECKLEYANUS**

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Plants. Cuttings of *Lophocereus schottii* (Engel.) Br. & R. (the "senita cactus"), *L. schottii* forma *monstrosus* Gates (the "totem pole cactus"), and *L. schottii* forma *mieckleyanus* G. Lindsey, as described by Lindsey [1]. *Source.* From authenticated plants growing in the Desert Botanical Garden of Arizona, Papago Park, in Phoenix, Arizona. *Previous work.* The presence of tetrahydroisoquinoline alkaloids in the genus *Lophocereus* is well documented [2–6].

Present work. A re-examination of *L. schottii*, using previously reported TLC screening [7,8], indicated no appreciable amounts of new alkaloids. Similar screening of two previously uninvestigated monstrose forms, *L. schottii* forma *monstrosa* and *L. schottii* forma *mieckleyanus*, showed identical alkaloid content. However, *L. schottii* forma *mieckleyanus* was quantitatively richest in alkaloids. $CHCl_3$ extraction and ion-exchange chromatography [7] of 775 g of freeze-dried, pulverized, and defatted *L. schottii* forma *monstrosus* yielded 74 mg of pilocereine (m.p. 175–176°, m.m.p. 174–175°; lit. 174–175°, IR, 0·01% yield) after refrigeration of the phenolic alkaloids in Et_2O and recrystallization from EtOAc. Surprisingly the non-phenolic fraction also contained pilocereine which substantiates the earlier reports of the cryptophenolic nature of this compound [3].

An identical extraction was conducted with 885 g of *L. schottii* forma *mieckleyanus*. Separating the alkaloids on neutral alumina (activated for 2 hr at 137°) with C_6H_6–Et_2O (1 : 1). Crystallization from EtOAc yielded 23 mg of pilocereine (m.p. 174–175°, m.m.p. 173–174°, reference m.p. 174–175°, IR, 0·005% yield). Lophocerine and traces of unidentified alkaloids were observed by TLC in the phenolic alkaloid fractions of all three plants. Due to the small quantities observed, attempts to crystallize additional alkaloids were not made.

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* Part XXV in the series "Cactus Alkaloids". For Part XXIV see Vanderveen, R. L., West, L. G. and McLaughlin, J. L. (1974) *Phytochemistry* **13**, 866.