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ISOLATION OF SAPOGENIN STRUCTURES FROM THE ROOTS OF LYSIMACHIA MAURITIANA LAM

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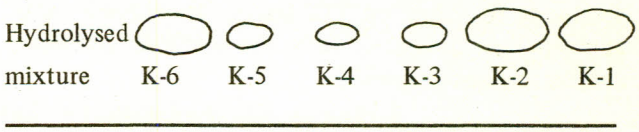
Abstract. Work on the sapogenin constituents of *Lysimachia mauritiana* Lam. has been carried out, and respective identification of two components with Camelliagenin A and Camelliagenin C are recorded.

Primulaceous roots have often been used as valuable plant expectorant. Among several kinds of root constituents, the saponins have been believed to be responsible for physiological activity, and this appears why Tschesche[1,2,3] and Yosioka[4,5] have extensively studied saponin and sapogenins from Primulaceous plants. Camelliagenin A has already been isolated from the fruits of *Lysimachia mauritiana* Lam., but no chemical evidence on the saponin and sapogenin constituents of roots of *Lysimachia mauritiana* Lam. has so far been reported in the literature.

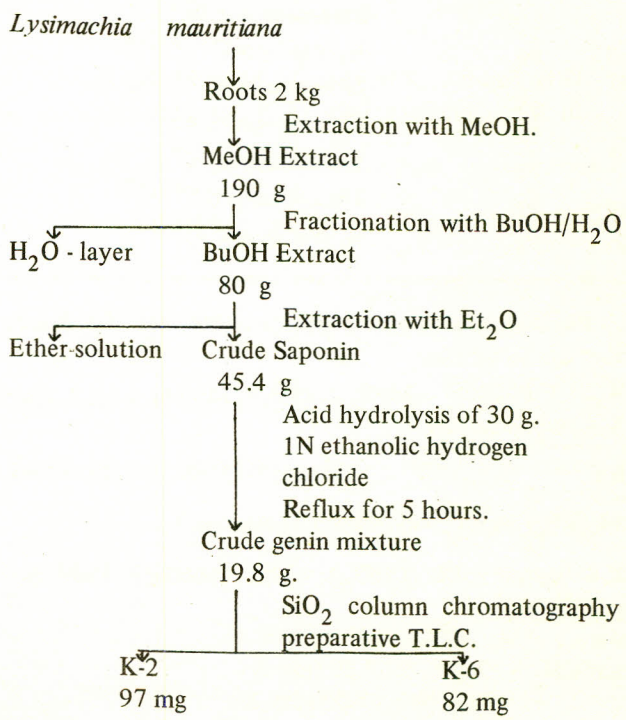
Experimental

The methanol extract of the roots of *Lysimachia mauritiana* Lam. were fractionated by n-butanol water mixture, and n-butanol soluble parts were treated with ether repeatedly, furnishing with crude saponin. The crude saponin was hydrolysed by refluxing 5 hr in 1 N ethanolic hydrogen chloride and a sapogenin mixture was obtained. Thin Layer Chromatography (TLC) of the hydrolysed genin mixture on silica gel G with $CHCl_3$: MeOH(10:1) as developing solvent and detected with $CeSO_4$ in 10% H_2SO_4, showed several triterpenoid compounds which were provisionally named as K-1, K-2, K-3 K-4, K-5 and K-6 according to their decreasing R_f values on TLC plate. The separation of the hydrolysed genin mixture was achieved on silica gel column which was eluted first with $CHCl_3$: MeOH (20:1) and then AcOEt : MeOH (20:1) ratio, but all the eluent fractions gave mixture of two or more constituents. Preparative TLC of the different column fraction were carried out on silica gel G plates with $CHCl_3$: MeOH (20:1) and sprayed with distilled water to mark the separation of various bands of constituents and thus chromatographically pure compounds were obtained. Two components viz K-3 and K-4 could not be isolated in sufficient quantity for further analysis. The respective identification of K-2 and K-6 are described in this paper. Whereas components such as K–1 and K–5 will be reported elswhere. Schemetic representation of isolation of constituents is also reported here.

Chart 1. TLC of sapogenin mixture



SiO_2 $CHCL_3$: MeOH (10:1), $CeSO_4$ - H_2SO_4 aq. soln.



Experimental Scheme

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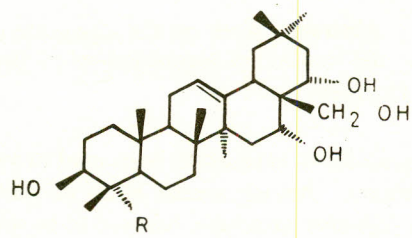
Crystallization was achieved from a mixture of MeOH : H_2O in case of K-1 and K-2 and n-hexane: acetone in case of K-5 and K-6 by keeping the solution containing the constituents at room temperature for two to three or more days till the crystal formation is completed.

These components were acetylated with 1-ml of acetic anhydride in 2.5 ml of pyridine, and the reaction mixture was poured into water and extracted with ether. On evaporation of the ether extract, the crude acetate was obtained.

Result

TLC showed that hydrolysed genin mixture was composed of six triterpenoids which were provisionally named K-1, K-2, K-3 K-4, K-5 and K-6 according to their decreasing R_f values on TLC plates. Hydrolysed genin mixture was compared with the available authentic samples as given in Table 1.

From the spectroscopic data recorded above it appeared that K-2 and K-6 were identical with Camelligenin A (dihydropriverogenin A[6,7,8]) and Camelliagenin C[6,7] respectively. The confirmation of the respective identities with the authentic specimens were established by mixed melting point determination, comparison of IR spectra, and reproducible values of NMR spectra and thin layer chromatographic behavior.



(I) R= CH_3 Camelliagenin A
(II) R = CH_2OH Camelliagenin C

TABLE 1. COMPARISON OF GENINS WITH AUTHENTIC SAMPLES

Abbreviation	Name of authentic samples	Solvent used in TLC	Solvent ratio	Remarks
Prim A	Primulagenin A[4]	$CHCl_3$: MeOH	20:1	
Cam A	Camelliagenin A[6,7,8]	" "	"	Identical with K-2
Cam C	Camelliagenin C[6,7]	" "	"	Identical with K-6
Cam D	Camelliagenin D[11]	" "	"	
R_1	R_1-barrigenol[12,13,14]	" "	10:1	
P_R	Protoaescigenin[15,16]	" "	"	
T_A	Theasapogenol A[10]	" "	"	
T_B	Theasapogenol B[9]	" "	"	
T_E	Theasapogenol E[11,17]	" "	"	
A_1	A_1-barrigenol[12,13]	" "	"	

Physical properties and spectrometric data of K-2 and K-6 are as follows:

K-2, M.P. 242° - 245°; IR (KB_r) (3450-br), 1635. cm^{-1}

K-6 and its acetate

K-6, m.p. 178° - 182°; (α) D+5° (C, 1.0; pyridine);

IR (KB_r) 3450_{br}.) (1700-w.) 1640w cm^{-1}

K-6 acetate: IR ($CHCl_3$) 1725, (1660w) 1600 w. (1250) cm^{-1}

NMR (60 Mc., $CDCl_3$ τ)

tert-CH_3 9.17 (3H, S.) 9.09 (6H, S)
9.03 (3H, S.) 9.00 (3H, S)
8.60 (3H, S.)

-$OCOCH_3$ 8.00 (6H, S.) 7.98 (6H, S)

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