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3-*EPI*KATONIC ACID FROM GUAR MEAL, *CYAMOPSIS TETRAGONOLOBA*

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Key Word Index—*Cyamopsis tetragonoloba;* Leguminosae; guar; seed meal; saponin; pentacyclic triterpene; 3-*epi*katonic acid; 11-deoxo-18β-liquiritic acid; 3β-hydroxyolean-12-ene-29-oic acid.

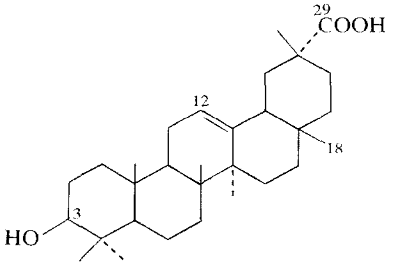
INTRODUCTION

Guar, *Cyamopsis tetragonoloba* L. (syn. *C. psoraloides*) is a drought-tolerant annual herb indigenous to the Indian subcontinent. The plant is also grown commercially in the drier areas of U.S., South Africa and Australia because the seeds are a source of the valuable guar gum, a galactomannan which is used in confectionery and cosmetics. After milling to remove the endosperm which contains most of the gum, the residual meal (45% protein) is used as a stock feed. However, the incorporation of guar meal in poultry diets is limited by its adverse effect on chick growth and on egg production. Verma [1] working at the Poultry Research Centre, showed that guar meal contained about 10% saponin and that the addition of cholesterol to a laying-hen diet containing guar meal improved egg production.

This paper reports on the isolation and identification of the major sapogenin obtained by acid hydrolysis of the saponin extracted from guar meal.

RESULTS AND DISCUSSION

Although the saponin has not been obtained in a pure crystalline state, acid hydrolysis of the crude product gave 5% by weight of ether-soluble material from which a crystalline acidic sapogenin, mp 283–284°, was isolated by recrystallization from acetone. The MS and ^{13}C NMR were consistent with those of a 3β-hydroxypentacylic triterpene acid, distinct from oleanolic acid. Comparison ot the mps and $[\alpha]_D$, of several derivatives of the guar sapogenin with those of 3-*epi*katonic acid [2] indicated a similarity. The identity of guar sapogenin was established as 3-*epi*katonic acid or 11-deoxo-18β-liquiritic acid **1** [mmp of acetate



1

methyl ester, ^{13}C NMR comparison [3], TLC in four solvents].

3-*Epi*katonic acid has not been previously isolated as a natural product but its epimer, katonic acid, occurs as a free triterpene in the heartwood of *Sandoricum indicum* (Meliaceae) [2].

EXPERIMENTAL

All mps are uncorr. MS (probe) were determined on an AEI MS 902 operating at 70 eV with a source temp. of 200°. Optical rotations were taken in $CHCl_3$. TLC was performed on Merck Si gel F 254.

Extraction and isolation of sapogenin. Guar meal (10.9 kg) was extracted with Me_2CO for 24 hr to remove lipids (740 g, 6.8%). Part of the residual meal (2.45 kg) was extracted with MeOH for 48 hr. On cooling the extract, a dark-brown gum (168.6 g) was deposited. The mother liquor was diluted with Me_2CO (4 vol.) to yield a pale yellow ppt. (143 g). TLC using *iso*PrOH–HCOOH–H_2O (70:6:24) showed that the 2 fractions contained the same 4 constituents; yield of crude saponin 12.7%. A sol of saponin (128.8 g) in 50% EtOH–1.7 M HCl (1.2 l.) was refluxed 4.5 hr. The reaction mixture was diluted to 3 l. and briefly boiled. Filtration afforded a black solid which was dried and extracted in a Soxhlet with Et_2O for 16 hr. The ether-soluble fraction (6.43 g, 5%) was recrystallized repeatedly from Me_2CO and finally from $CHCl_3$–MeOH (1:2) to yield colourless plates, mp 283–284°; $[\alpha]_D^{23}+61°$; MS *m/e*: 456.3639 M^+ (rel. int. 2.4); $C_{30}H_{48}O_3$ requires MW 456.3603.

Derivatives of the sapogenin. Methyl ester, mp 203–205°; $[\alpha]_D^{23}+55°$ (methyl *epi*katonate, mp 199–200°; $[\alpha]_D+58°$[2]); MS *m/e* (ret. int.): 470 M^+ (3.7). Acetate of methyl ester, mp 246–247°; $[\alpha]_D^{23}+59°$ (acetate of methyl *epi*katonate, mp 245–246°; $[\alpha]_D+54°$ [2]); mmp with 11-deoxo-18β-liquiritic acid methyl ester acetate, mp 245–247°: no depression. MS *m/e* (rel. int.): 512 M^+ (4.5) 262 (100), 249 (21.4): retro-Diels–Alder. ^{13}C NMR (25.2 MHz, $CDCl_3$): δ 38.3, 23.6, 80.9 (*d*, C-3), 37.7, 55.3, 18.3, 32.6, 39.9, 47.6, 36.9, 23.6, 122.7 (*d*, C-12), 144.1 (C-13), 41.7, 25.9, 27.0, 32.5, 46.1, 40.5, 42.7, 29.1, 36.0, 28.1, 16.9, 15.6, 16.9, 25.9, 28.1, 19.3, 51.6 (*q*; $COO\underset{\cdot}{C}H_3$), 170.7 (*s*; $O\underset{\cdot}{C}OMe$), 179.0 (*s*; $\underset{\cdot}{C}OOMe$: C-29) 21.2 ppm ($OCO\underset{\cdot}{C}H_3$). R_fs: $CHCl_3$, 0.61; toluene–EtOAc (8:2), 0.57; di-isopropyl ether-$CHCl_3$ (1:1), 0.55, cyclohexane–EtOAc (1:1), 0.66. Acetate, mp 297–299° decomp; $[\alpha]_D^{23}+52°$; MS *m/e* (rel. int.): 480, M − 18 (22.1), 438, M − 60 (7.2).

3-*Ketone.* Guar sapogenin methyl ester was oxidized with CrO_3–dimethyl-pyrazole [4]. The pure ketone was obtained from MeOH as lustruous needles, mp 161–162°; $[\alpha]_D^{25}+74°$ (methylkatononate, mp 157–158°; $[\alpha]_D+80°$ [2]).

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