SHORT COMMUNICATIONS

TRITERPENOIDS
Part II. Another Sapogenin from Fagonia cretica Linn. (Zygophyllaceae)

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In an earlier communication[1] we described the isolation of two sapogenins, viz., Fagogenin and Genin A from *Fagonia cretica* Linn. We now report the isolation of a third genin tentatively designated as Genin B. The present method of isolation is some-what different from that adopted in case Fagogenin and Genin A.

The total neutral sapogenins (54 g), obtained by the method described earlier,[1] were extracted with ether in a soxhlet apparatus and the extract freed from solvent. The residue (21.5 g), on crystallisation from benzene, yielded crude Fagogenin (13.7 g), m.p. 290–95°. The benzene mother-liquor was freed from benzene and the residue (7.8 g) dissolved in light petroleum and chromatographed on a column of acid alumina. The column was eluted successively with light petroleum, light petroleum–benzene, benzene, benzene–chloroform and chloroform. The fractions collected from the beginning till light petroleum–benzene (1:3) was used for elution, gave crude Genin A (1.4 g) which, on crystallisation from methanol, had m.p. >330°. Next, elution with pure benzene and benzene-chloroform (9:1) yielded crude Genin B (1.03 g), m.p. 228–34°. After this, an oil (1.1 g) and Fagogenin (3.3 g), m.p. 290–95°, were successively eluted.

The crude Genin B, on several recrystallisations from methanol, was obtained pure white needles, m.p. 247–48°, $[\alpha]_D^{35}$ + 21.66° (c=0.60, $CHCl_3$). The compound analysed for the molecular formula, $C_{50}H_{50}O_2$ (Found: C, 80.66 and H, 11.29%; $C_{30}H_{50}O_2$ requires: C, 81.44 and H, 11.31%). The IR spectrum of the compound in KBr (Fig. 1) showed only hydroxyl absorption but no carbonyl. The compound produced a violet colouration with Liebermann–Burchard reagent. With acetic anhydride and pyridine at room temperature, Genin B gave a diacetate which crystallised from methanol in colourless, shining needles m.p. 218°, $[\alpha]_D^{33}$ + 24.8° (c=0. 884, $CHCl_3$), $C_{34}H_{54}O_4$ (Found: C, 77.41 and H, 9.87%; $C_{34}H_{54}O_4$ requires: C, 77.56 and H, 10.26%). The IR spectrum of the acetate in KBr showed a strong peak at 1734 $cm.^{-1}$ due to the ester carbonyl and no hydroxyl absorption was present. From the analytical data, melting point and optical rotation of Genin B and its diacetyl derivative, it seems that

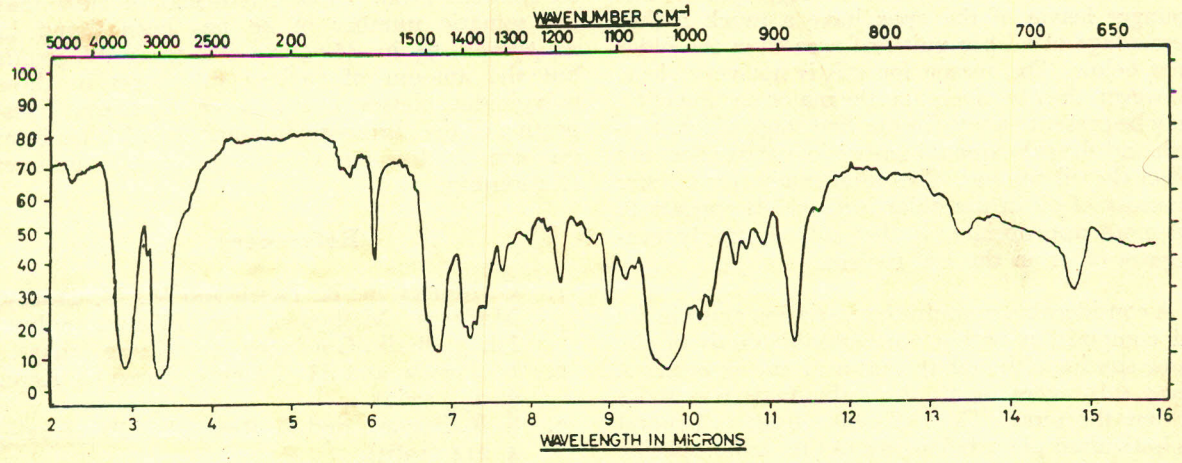

Fig. 1.—IR spectrum of Genin B in KBr.

Genin B is very probably identical with the triterpenic dihydric alcohol, Betulin[2] (lup-20 (30) en-28, 3β-diol); but further evidence must be awaited before a final conclusion is drawn. Further work on Genin B is in progress.

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PROTEIN VALUE OF CRUST AND INTERIOR PORTION OF THE LEAVENED BREAD

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Wheat supplies the major portion of calories and nutrients in the diet of the people of West Pakistan. Since wheat products are always baked before consumption, the authors considered it of interest to determine the effect of baking on the protein value.

Two dozen bread loaves, weighing about half pound each, were made of wheat flour in the Experimental Kitchen of these Laboratories. They were divided into two portions, the crust and interior portion of the bread. The soft portion was broken into small pieces and dried at room temperature (28°C) to a moisture content of about 15% which took 4–5 hours. It was then ground into a course powder for feeding rats. The crust portion was also similarly treated.

Nitrogen, calories, net protein utilization operative (NPU Op) and net dietary protein calories% (NDp Cals %) were determined according to the methods described earlier.[1,2] Available lysein was estimated according to the method of Carpenter and Ellinger.[3]

Results of analysis are shown in Table 1. Although the protein content of the crust and interior portion of the bread was the same, there was a marked decrease in the NPU of the crust with consequent lowering of the NDp Cals%. The NDp Cals% of the interior portion of the bread was almost similar to that of wheat flour, whereas about 50% reduction in the protein value of crust as compared with the interior portion of the bread had occurred. About 15% less available lysine in the crust than that of the corresponding flour has been reparted [4,5] which is in agreement our results. Since Carpenter *et al.*[6] have shown a correlation between available lysine and protein nutritional value of a number of food stuffs, the available lysine content of the crust might lead to the conclusion that very little damage to wheat protein in the formation of crust is caused which is not confirmed by our observations. It is probable that besides damage to lysine some other (toxic?) substances are produced in the curst as a result of high temperature during the baking process which adversely affect the NPU. Thus one should be careful in interpreting the results of chemical analysis unless these are confirmed by biological tests which take into account other factors affecting the utilization of nutrients in the body. The above findings also indicate the harmful effect of excessive baking which should be avoided.

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TABLE 1.—ANALYSIS OF WHEAT FLOUR, CRUST AND INTERIOR PORTION OF THE LEAVENED BREAD.

	Available lysine mg/gN	Protein %	Calories 100 g	Protein calories %	NPU* (Op) %	NDP Cals. %
Wheat flour	129.4	10.1	360	11.2	50.2	5.6
Crust	109.0	10.0	360	11.1	26.2	2.9
Interior portion	125.0	10.1	365	11.1	53.2	5.9

* Mean values of duplicates containing 4 rats each.

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ACID CATALYSED REACTIONS OF 5α-MERCAPTOSTEROIDS

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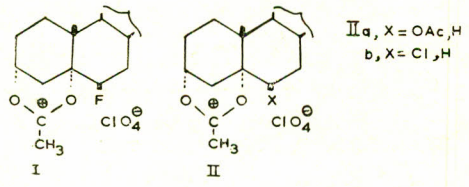
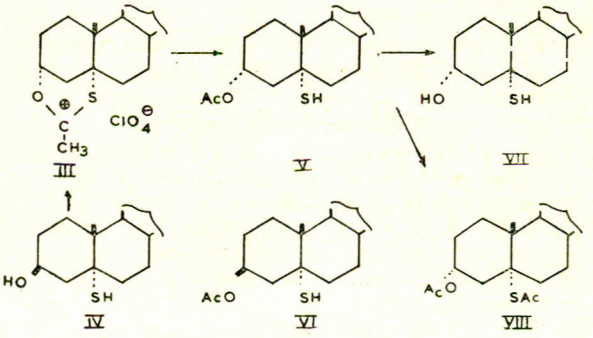
Recently 3α, 5α-acetonium ion perchlorate (I) has been prepared by the treatment of 3β, 5α-dihydroxy-6β-fluoro-cholestane with acetic anhydride in the presence of perchloric acid.[1] 6β-Acetoxy-and 6β-chloro-3β, 5α-dihydroxy-cholestanes also gave the corresponding 3α, 5α-acetonium ion perchlorates (II a, b) in the presence of sulphuric acid.[2,3]



Similarly we have isolated an ether-insoluble 3α-oxa-5α-mercapto-acetonium ion perchlorate (III) in 89% yield when 3β-hydroxy-5α-mercapto-cholestane[4] (IV) was reacted with perchloric acid and acetic anhydride in the absence of sulphuric acid. 3β-Acetoxy-5α-acetyl-mercapto-cholestane[4] also gave the perchlorate III in the same manner. It has m.p. 191–192° (decomposed); ν_{max}^{KBr} 1075 cm^{-1} (ClO_4-). It hydrolysed rapidly with water and furnished 3α-acetoxy-5α-mercapto-cholestane (V) m.p. 155°; ν_{max}^{KBr} 1740 and 1230 cm^{-1} (OAc). It gave a depression of melting point when mixed with an authentic sample of 3β-acetoxy-5α-mercapto-cholestane (VI). Alkaline hydrolysis of 3α-acetoxy-5α-mercapto-cholestane afforded 3α-hydroxy-5α-mercapto-cholestane (VII), m.p. 132 — 34°; ν_{max}^{KBr} 3450 cm^{-1} (OH) and 2550 cm^{-1} (SH). Treatment of 3α-acetoxy-5α-mercapto-cholestane (V) with acetic anhydride in the presence of perchloric acid for 8 min gave 3α-acetoxy-5α-acetylmercapto-chlolestane (VIII), m.p. 200-201°; ν_{max}^{CCl4} 1697 and 1120 cm^{-1} (SAc), 1745 and 1240 cm-1 (OAc).



Further work on "acid catalysed reactions of 5α-mercaptosteroids" is in progress.

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