HYDROLYZED GINSENG-SAPONIN QUATERNARY;

A NOVEL CONDITIONING AGENT FOR HAIR CARE PRODUCTS

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SUMMARY

A new quaternary ammonium compound, hydrolyzed ginseng-sapoin quaternary (HGSQ), from hydrolyzed Korean ginseng-saponin and 2, 3-epoxypropyltrimethyl ammonium chloride has been developed as a conditioning agent for hair care products. This structure has the hydrophilic group from the introduced cationic and the hydrophobic group from the aglycone of ginseng saponin. Its cationic site allows the molecule to be more substantive than ginseng saponin. Its properties: surface tension, conductivity, critical micelle concentration, eye irritation, sorption onto hair, force reduction (%) for 20% extension and moisture retention effect comparing with the commercial standards. Also half-head tests of HGSQ-containing shampoo were carried out to compare the conditioning effects in shampoos.

1. INTRODUCTION

Ginseng has very good effects on skin and hair (1). But it has poor adherent property in rinse-off skin and hair care products. Skin and hair have an overall negative charge at normal pH's, they are ideal for interaction with cationic materials. Cationics are substantive because of the interaction of their positive charge with the substrate's negative charge. The cationic material improves the texture of dry hair and softens it. It neutralizes the apparent anionic charge of the hair and therefore eliminates static flyaway effect (2). Its positive charge on the cationic helps the hair hold onto water and increase the hydrophilic nature of hair. The key to its effects is the substantivity to hair (3). It was necessary for us to find out the more effective method of using the precious ginseng in cosmetics. In this study, we have improved the substantivity of ginseng saponin to hair by introducing the cationic group to the aglycone of ginseng saponin.

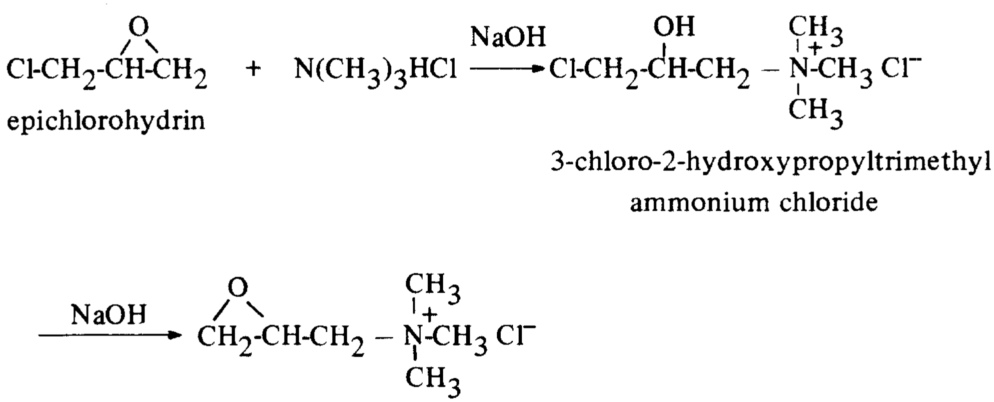
2. PREPARATION OF HYDROLYZED GINSENG-SAPONIN QUATERNARY

2-1. Hydrolysis of ginseng saponin

Ginseng saponins were prepared from Korean ginseng by Pacific Chemical Co. Ltd. (Korea) and purified according to the procedure by Joo (4). Ginseng saponin (150g) was dissolved in water (500ml) at 40°C, and conc. H_2SO_4 (110g) was dropped into the reaction vessel with efficient stirring and standed for 1 hr at 55°C. The resulting reaction mixture was filtered and dissolved in chloroform. The organic layer was washed with sodium bicarbonate (2%) and water, and removed the chloroform on a rotary evaporator to give yellow solid. The solid was recrystallized from acetone-water. The degree of reaction was checked by TLC on silica gel. R_f = 8.9 (broad) (solvent: chloroform/methanol/water = 65/35/10, lower phase). The nmr spectrum of hydrolyzed ginseng-saponin (HG S) showed no sugar peaks. (Figure 4)

2-2. Quaternization of HGS

As shown in Figure 1, the quaternization of HGS was achieved by etherifying HGS with quaternary epoxide (2,3-epoxypropyltrimethyl ammonium chloride). The synthetic procedure of quaternary epoxide was described below (5).



60g of HGS was suspended in 300ml of isopropyl alcohol. 3.5 fold excess of quaternary epoxide was slowly added to the solution of HGS, followed by an equimolar amounts of sodium hydroxide. The reaction was continued for 8 hr at 55°C. After reaction was completed as judged by TLC (Figure 2), the reaction solution was neutralized with 4ml of acetic acid for 30 min, and then concentrated to syrup on the rotary evaporator. The crude product was applied to a column of Sephadex LH-20 (Pharmacia, Sweden) and eluted with methanol. Fractions were collected and every fraction was checked by TLC on silica gel (solvent; chloroform/ methanol/water = 13: 7: 2, lower phase) using Dragendorff reagent (6). After pooling the main product fractions, methanol was evaporated under reduced pressure. The resulting solid product was also analyzed by paper eletrophoresis. It showed positive character. Nitrogen analysis of purified HGSQ indicated that it contained 2.4% nitrogen, which correspond to a substitution level of 1.73mmol/g. The structure of HGSQ was confirmed by nmr spectrum (Figure 3, 4 and 5). Average molecular weight of HGSQ determined by the freezing point depression and nitrogen analysis was about 557.

3. PHYSICAL PROPERTIES OF HGSQ

The standard commercial materials consisted of ginseng saponin, CTAC (Ammonyx CETAC, Onyx, U.S.A.), STAHP (Crotein Q, Croda, England).

3-1. Experimentals

3-1-1. Critical Micelle Concentration (CMC)

1) surface tension

Surface tensions of aqueous solutions of HGSQ, ginseng saponin, CTAC and STAHP at 10^{-5} to 2% (w/w) concentrations were measured by du Nouy Tensiometer (model 215 Fisher Scientific, U.S.A.) at 20 ± 2°C.

2) conductivity

Conductivities of HGSQ comparing with CTAC at 20 ± 2°C aqueous solutions of 10^{-5} to 10^{-1}% (w/w) concentrations were measured by conductometer (model 518, electrode model EA 608-C, Metrohm Herisau, Switzerland).

3-1-2. Eye irritation

0.5% active solutions were prepared for HGSQ, ginseng saponin, CTAC, STAHP and stearyltrimethyl ammonium chloride (STAC). Six normal healthy albino rabbits were used in this experiment. The scores were recorded according to the Draize scoring ocular lesions (7).

3-1-3. Sorption onto hair

Virgin black hairs from female Korean aged 20–30 were collected (25cm long). Enough hair tresses (1g and 4cm long) were prepared and shampooed with 1% Triton X-100 aqueous solution, rinsed with distilled water and dried at 20 ± 2°C, 60 ± 4% RH overnight. Half of hair tresses were bleached by the following procedure;

Bleaching solution A; 5ml NH_4OH (28%) H_2O to 1 liter

Bleaching solution B; 20 volumes (6%) H_2O_2

Equal part of solution A and B were mixed at 20 ± 2°C. Each hair tress was put into the beaker of 50ml mixed bleaching solution for given times. After bleaching, the tresses were shampooed twice with 1% Triton X-100 solution and rinsed twice with distilled water. The tresses were conditioned in a humidity controlled chamber to 60 ± 4% RH at 20 ± 2°C. 1g of hair tress was immersed in 100ml Erlenmeyer flask with 50ml of sample solutions of HGSQ and other test materials at 20 ± 2°C for given concentrations and times in a shaker.

Determination of sorption amounts

1) HGSQ and CTAC

The sorbed HGSQ and CTAC were extracted with 30ml of 80% methanol solution three times from the treated hair tresses respectively. The extracted solution from hair tress was evaporated in vacuum. The residue was dissolved with small amount of water and made up to about 40ml with water and about 1ml of 0.1% (w/w) solution of picric acid in 0.002M sodium hydroxide added. 20ml of distilled chloroform was added to the whole solution and shaken for 5 min. The organic layer was then separated and centrifuged at 3500 rpm for 5 min. The resulting picric acid-quaternary ammonium compound complex in chloroform was determined at 360nm using spectrophotometer (Series 5000, Ceil Instruments, England) (8, 9, 10).

2) ginseng saponin

The sorbed ginseng saponin was extracted with 30ml of 80% methanol solution three times from the hair tress treated in test ginseng saponin solution. The solution extracted from hair tress was evaporated in a rotary evaporator. The residue was dissolved into 2ml of 80% methanol solution. The sample solution was eluted with CH_3CN: H_2O(28.5:71.5) on μ - Bondapak C18 (3.9mm x 30cm) and the absorbance of the ginseng saponin was determined at a wavelength of 203nm (flow rate: 3.0ml/min) (11).

3) STAHP

The STAHP sorbed hair was chopped into small pieces and put into a test tube and added 10ml of 1:1 mixture of concentrated hydrochloric acid and propionic acid. The sample was frozen in a bath of dry-ice and acetone (-78°C). The tube was sealed off at the constriction, still under vacuum and standed on oven for 24hr at 110°C. The hydrolysate was lyophilized. The amount of STAHP was determined by amino acid analysis.

3-1-4. Force reduction (%)

Hairs were bleached and rinsed as the same way in sorption test. The hairs with diameter between 80 and 90μm were selected microscopically. Both ends of hair were protected from damage by a Scotch filament tape (Figure 6).

First, for bleached hairs (20 pieces) conditioned at 60 ± 4% RH and 20 ± 2°C for 10hr, the force for 20% extension was measured and the bleached hairs were relaxed overnight (15hr) in the water and treated with 50ml solutions of test materials at given concentrations (0.05 to 5%), immersion times (10 to 180min and 15hr) and rinsed twice with 50ml distilled water and conditioned again at 60 ± 4% RH and 20 ± 2°C for 10hr. Next, the force for 20% extension of bleached hairs treated with solutions of test materials were measured again.

Rheo Meter (model 200-2J Fudo Kogyo Co. Japan) with multipen recorder (Figure 6) was used to measure the force reduction (%) at 20 ± 2°C, 60 ± 4% RH. Under the conditions of initial hair length 50mm, the rate of extension was 5cm/min and full scale was 200gf.

The % reduction in force required to extend a fiber 20% after treatment was calculated using the following equation.

$$\text{Force reduction (\%)} = \frac{F_0 - F_1}{F_0} \times 100$$

Where F_0 is the initial force required to extend a fiber 20% and F_1 is the force required to reextend the same fiber to 20% after treatment (12).

3-1-5. Moisture retention effect

2g of hair tresses were treated with 50ml solution of 0.5% test materials at 20 ± 2°C for 15hr, rinsed with 50ml distilled water twice and finally conditioned at given relative humidities (20 to 95%) for 10hr at 20 ± 2°C.

Under the same conditions moisture retention effects of HGSQ itself was also compared with propylene glycol, glycerine and commercial standards. Measurements of weight at given conditions were carried out on an electrobalance to ± 0.1mg accuracy in humidity controlled room at 20 ± 2°C.

$$\text{Moisture absorption regain (\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

W_0 : weight at initial condition (20 ± 4% RH, 20 ± 2°C)
W_1 : weight at given conditions

3-2. Results and Discussions

3-2-1. Critical Micelle Concentration (CMC)

The test results are shown in Figure 7 and 8. The CMC value of HGSQ by surface tension at 20 ± 2°C was 0.01% (w/w), which was almost the same value by conductivity method. Ginseng saponin had the CMC value of 1.0% (w/w), which is much larger than that of HGSQ and almost the same value by Kim et al (13). By these facts, we found that HGSQ had a reasonable surface activity. Its small CMC value maybe comes from the large and particular hydrophobic group, the aglycone of ginseng saponin.

3-2-2. Eye irritation

As shown in Figure 9, HGSQ was proved to be less irritating than the other cationics and ginseng saponin. HGSQ, even though it is a quaternized compound from ginseng saponin, is less irritating than ginseng saponin itself. It is generally considered that cationics have higher irritancy than nonionics and anionics. Using the Chamber Scarification Test for assessing irritancy, Frosch and Kligman found that the general decreasing order of irritancy is as follows: cationics > anionics > nonionics (14). But it is very interesting that HGSQ showed less irritancy than gineng saponin which is thought to be extremely non-toxic (15), and much less irritancy than CTAC and STAC at 0.5%. Maybe it comes from the characteristic property of ginseng saponin aglycone (4).

3-2-3. Sorption onto hair

The test results are shown in Figure 10, 11, 12 and 13. In Figure 10, for virgin hair at low concentration of 0.05 to 0.5% sorbed amount of HGSQ was much more than others but at above 0.5%, CTAC showed the highest sorption value. Both HGSQ and CTAC were no more sorbed at the concentrations of above 1.0%. But in case of saponin, the sorbed amount was increased according to the concentration to 3.0% (w/w). HGSQ showed much higher sorption amount onto hair than ginseng saponin in this condition. The sorbed amount onto bleached hair was much higher than onto virgin hair as expected (Figure 11). HGSQ showed much higher sorption amount at 0.05% than others and over 1.0% (w/w) its sorption amount was slightly decreased by increasing the concentration up to 3.0% (w/w). CTAC also showed the same results. The sorption amounts onto virgin hair and bleached hair at given immersion times (15 to 180 min) are shown in Figure 12 and 13. HGSQ showed higher sorption amounts than ginseng saponin. These results explain the higher substantivity of HGSQ than ginseng saponin in this condition.

3-2-4. Force reduction (%)

In Figure 14, force reduction (%) for 20% extention at given concentrations are shown. HGSQ showed much lower value of force reduction (%). This means HGSQ modify the structures of bleached hair more effectively than the other materials tested. Force reduction (%) decreased gradually by the increase of the concentration of HGSQ. Force reduction (%) at given immersion times are also shown in Figure 15. HGSQ also showed much lower value than three others, but its value was not decreased after 60 min immersion. But in case of ginseng saponin and CTAC, the values were decreased until to 120 min. Force reduction (%) at given bleaching times are shown in Figure 16. Force reduction (%) was rapidly increased according to the bleaching time. Of them, HGSQ showed lower values of force reduction (%), which means HGSQ has more effective modification effect on the tensile properties of damaged hair than others tested. This is maybe possible by the sorption of HGSQ into hair followed by the binding of HGSQ with amino acids, cysteic acid, in the hair cortex.

3-2-5. Moisture retention effect

Moisture absorption regain (%) isotherms for virgin hair itself and virgin hair treated with HGSQ and commercial standards were shown in Figure 17. It showed that HGSQ treated hair had much higher moisture absorption regain (%) than others, especially at high RH. Untreated virgin hair showed lowest value of the materials tested. Also moisture absorption regain (%) was measured for bleached hair itself and bleached hair treated with HGSQ, ginseng saponin, CTAC and STAHP, and the results are shown in Figure 18. Bleached hair treated with HGSQ showed the highest moisture absorption regain (%) especially above 40% RH. CTAC showed a little higher moisture absorption regain (%) on bleached hair than ginseng saponin and STAHP. In order to confirm the effect of HGSQ on moisture absorption regain (%) of hair, moisture absorption regains (%) of glycerine,propylene glycol, HGSQ, STAHP, ginseng saponin, virgin hair and bleached hair themselves were measured as shown in Figure 19. Virgin hair showed higher moisture absorption regain (%) than bleached hair.

HGSQ showed higher moisture absorption regain (%) than STAHP, CTAC, ginseng saponin, virgin hair and bleached hair, but lower value than glycerine and propylene glycol. HGSQ showed very similar value to that of propylene glycol at 80% RH. By these results we found that HGSQ itself had good moisture retention effect and made hair retain much moisture for damaged hair.

4. EVALUATION OF HGSQ-CONTAINING SHAMPOO

Experimental

For this study, we wanted a clear simple formula with as few ingredients as possible so as not to interfere with the conditioning properties of the test materials during their evaluation. Following simple shampoo formula which foam and clean well was used.

SHAMPOO FORMULATIONS

INGREDIENTS	A	B	C	D	E
SLES (30%)	40.0	40.0	40.0	40.0	40.0
COCOAMPHOCARBOXY-PROPIONATE (70%)	10.0	10.0	10.0	10.0	10.0
LAUROYL MYRISTOYL DEA	5.0	5.0	5.0	5.0	5.0
HGSQ	2.0	–	–	–	–
GINSENG SAPONIN	–	2.0	–	–	–
CTAC (25%)	–	–	2.0	–	–
STAHP	–	–	–	2.0	–
PROPYLENE GLYCOL	3.0	3.0	3.0	3.0	3.0
METHYL PARABEN	0.2	0.2	0.2	0.2	0.2
CITRIC ACID to pH 6.0	q.s.	q.s.	q.s.	q.s.	q.s.
PERFUME	q.s.	q.s.	q.s.	q.s.	q.s.
DEIONIZED WATER to	100.0	100.0	100.0	100.0	100.0

Five shampoos were prepared for the half-head test (16) involving 40 subjects. The subjects were all female aged 15-40. Half of them had permed hair. The effects of shampoo with HGSQ evaluated in regard to combability, feel of wet and dry hair as well as gloss and antistatic effects of dry hair. The hair was parted in the middle and combed out. One side was wetted, then washed with a measured amount of one of the shampoos. The other side was also wetted and washed with a measured amount of the other shampoo. At this point, foam quality and quantity were observed. Then the head was rinsed and washed again in the same manner. After the final rinse, wet combability and feel were evaluated. All 40 subjects were divided by 4 groups and 5 test shampoos were tested for the subjects. After drying slowly, the combability, feel, gloss and antistatic effect state were evaluated by the subject and the operator twice. Also these items were checked again 24hr later. The final decision on the effects of dry hair was made after checking both states; just after drying and 24hr later. In this half-head test, the assessment of shampoo A containing HGSQ was made by comparing with other shampoos, B, C, D and E.

Results and Discussions

The results of half-head test are shown in table I. The numbers mean the chosen times by the subjects and the operator. As shown in table I, shampoo A containing HGSQ was a very attractive product. In washing step, it gave rich and dense foam to the hair. The wet feel of shampoo A was similar to those of shampoo B and C, but superior to that of shampoo E. Wet combability of shampoo A was better than shampoo D and E, and similar to those of shampoo B and C. In dry hair, it showed excellent properties required for conditioning shampoo; soft feel, good combability, good sheen, and proper antistatic effect. These maybe come from the unique properties of HGSQ: high moisture retention effect, high sorption capacity onto hair due to its cationic character.

5. CONCLUSIONS

1. CMC value of HGSQ was 0.01% (w/w) which is much lower value than those of ginseng saponin, 1.0% (w/w) and CTAC, 0.1% (w/w).
2. HGSQ is less irritating than ginseng saponin and much less irritating than CTAC and STAC.
3. HGSQ shows better substantivity than ginseng saponin.
4. Force reduction (%) of HGSQ is much lower than those of the others tested.
5. Moisture retention effect of HGSQ on hair is very high comparing with those of CTAC, ginseng saponin and STAHP.
6. HGSQ shows good conditioning effects in a shampoo formula.

ACKNOWLEDGEMENT

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Table I. Half-head test results by subjects and operator.

GROUP		1		2		3		4	
PART		LEFT	RIGHT	LEFT	RIGHT	LEFT	RIGHT	LEFT	RIGHT
SHAMPOO		A	B	C	A	A	D	E	A
WET HAIR	FEEL	12	8	8	12	10	10	9	11
	COMBABILITY	11	9	9	11	13	7	4	16
DRY HAIR	FEEL	10	10	7	13	14	6	3	17
	COMBABILITY	12	8	7	13	13	7	4	16
	SHEEN	11	9	9	11	15	5	2	18
	ANTISTATIC EFFECT	12	8	10	10	16	4	4	16
WET HAIR TOTAL		23	17	17	23	26	14	13	27
DRY HAIR TOTAL		45	30	33	47	48	22	13	67
TOTAL		68	52	50	70	71	39	26	94

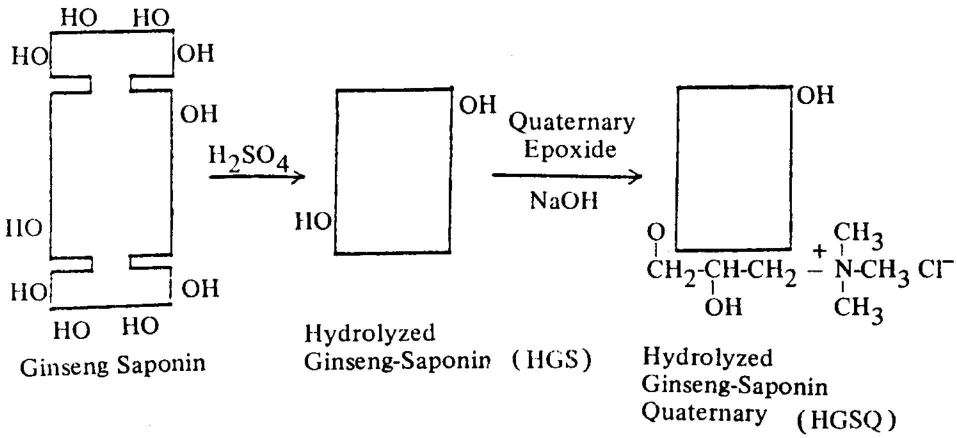


Figure 1. The preparation of HGSQ

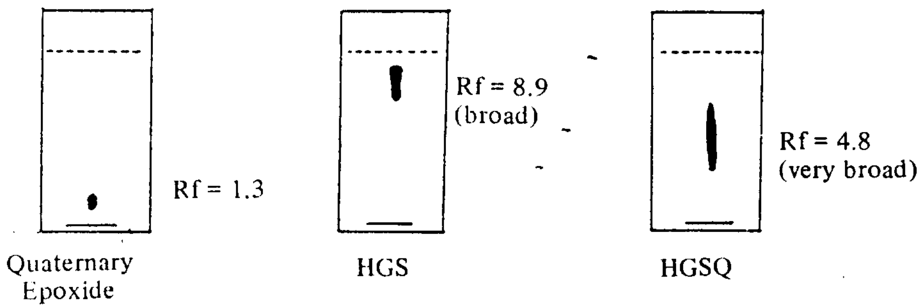


Figure 2. Thin Layer Chromatography (Silica gel 60F 254)
Solvent; $CHCl_3$-MeOH-H_2O (65:35:10), lower phase

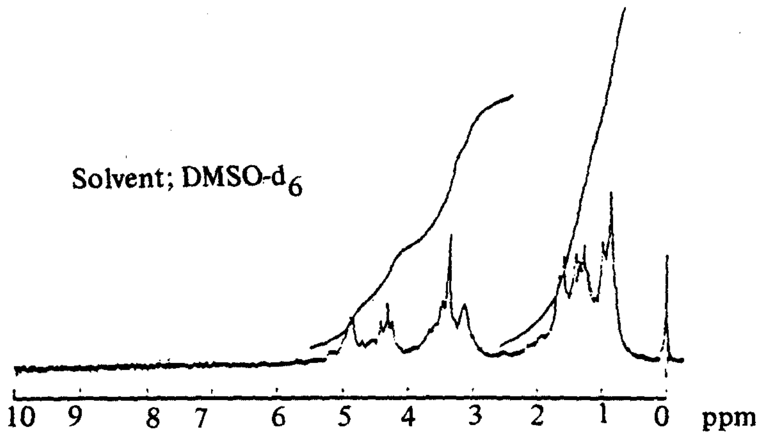


Figure 3. The nmr spectrum of ginseng saponin

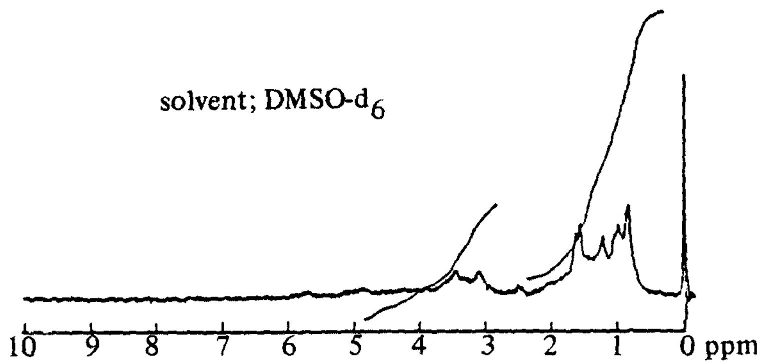


Figure 4. The nmr spectrum of HGS

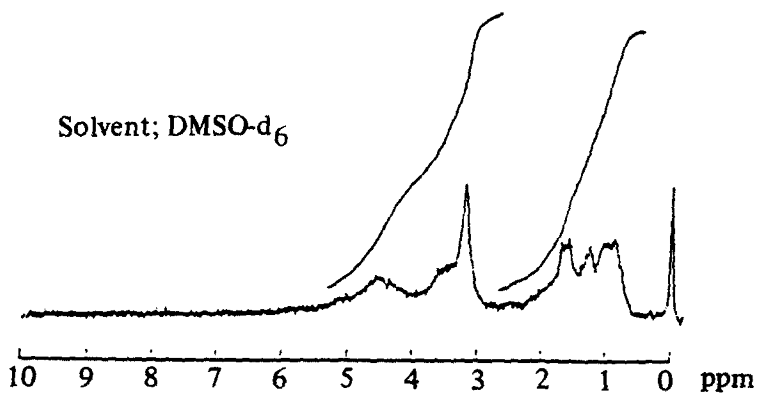
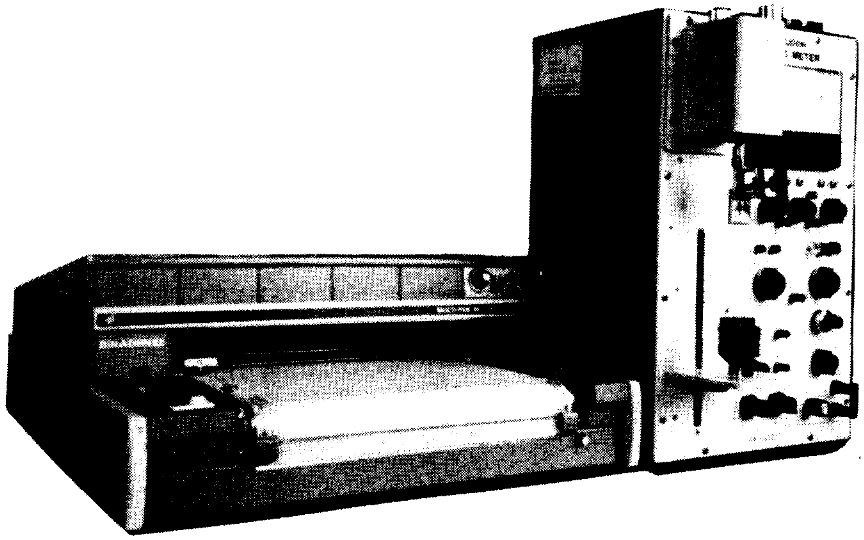
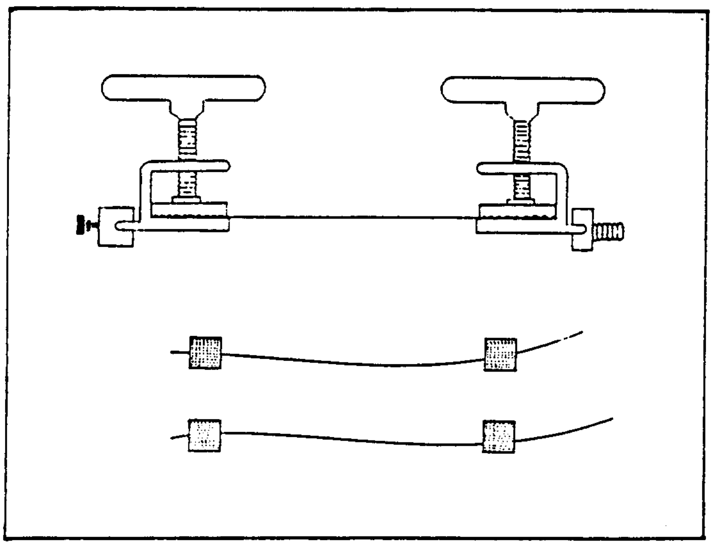


Figure 5. The nmr spectrum of HGSQ



(a)



(b)

Figure 6. (a) Rheo meter; (b) hair sample and clamp

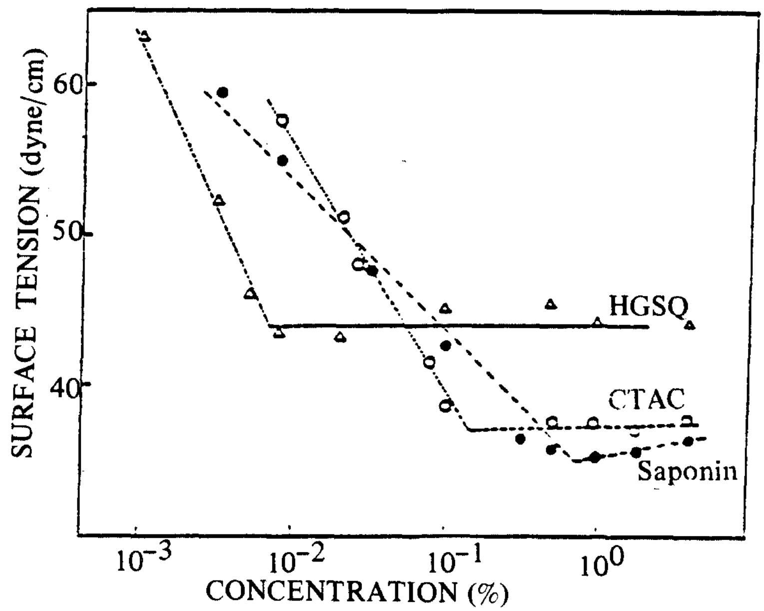


Figure 7. The effect of concentration on surface tension (temp. 20 ± 1°C)

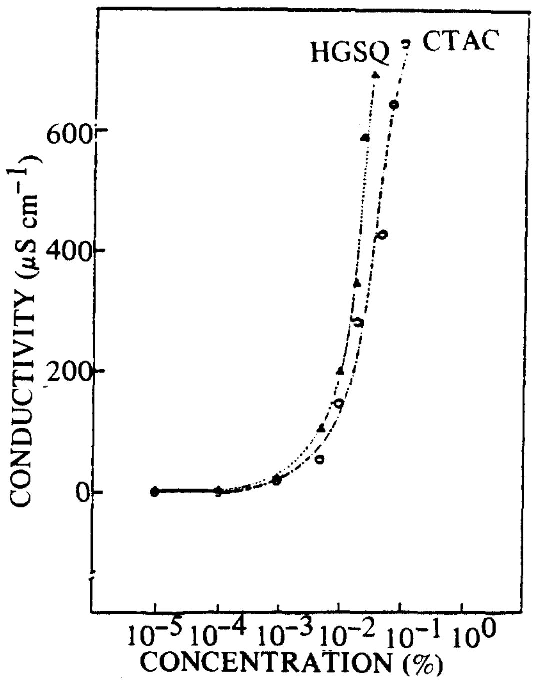


Figure 8. The effect of concentration on conductivity (temp. 20 ± 1°C)

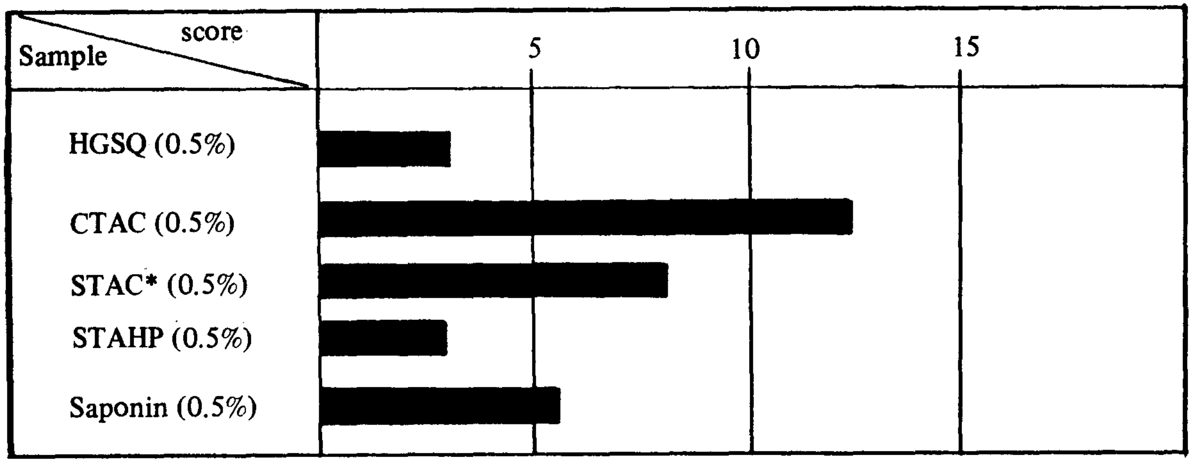


Figure 9. Draize eye irritation scores
(*: STAC=stearyltrimethylammonium chloride)

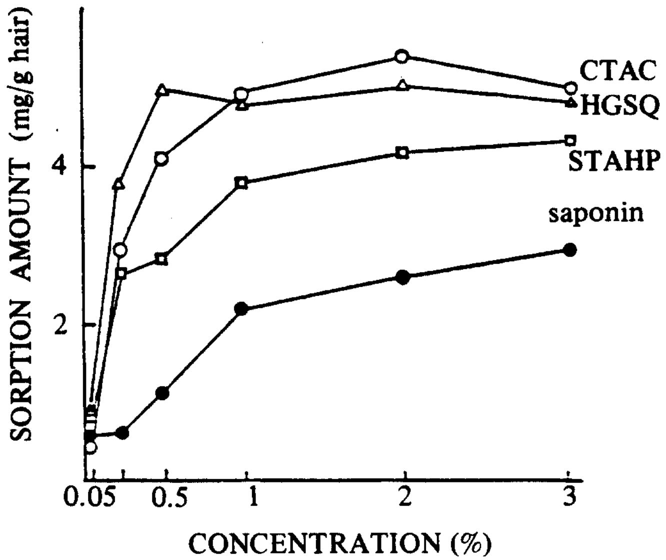


Figure 10. The effect of concentration on sorption amount of CTAC, HGSQ, saponin and STAHP into virgin hair (immersion time 3hr; temp. 20 ± 2°C; PH. 6.0 ± 0.1)

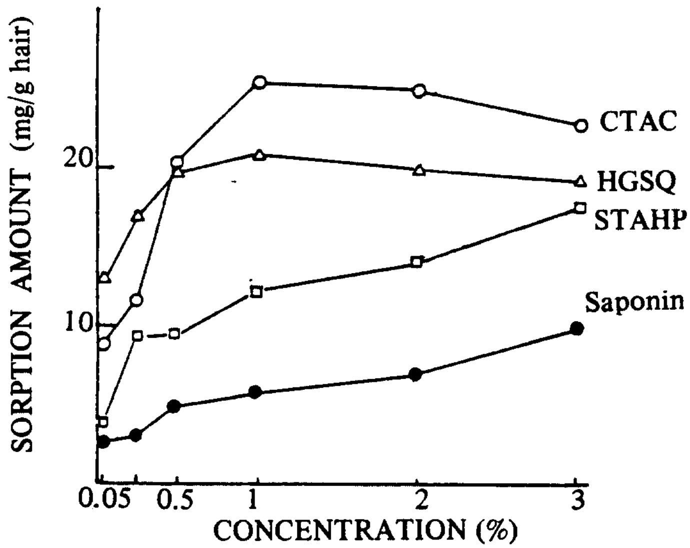


Figure 11. The effect of concentration on sorption amount of CTAC, HGSQ, saponin and STAHP into bleached hair (immersion time 3hr; temp. 20 ± 2°C; PH. 6.0 ± 0.1)

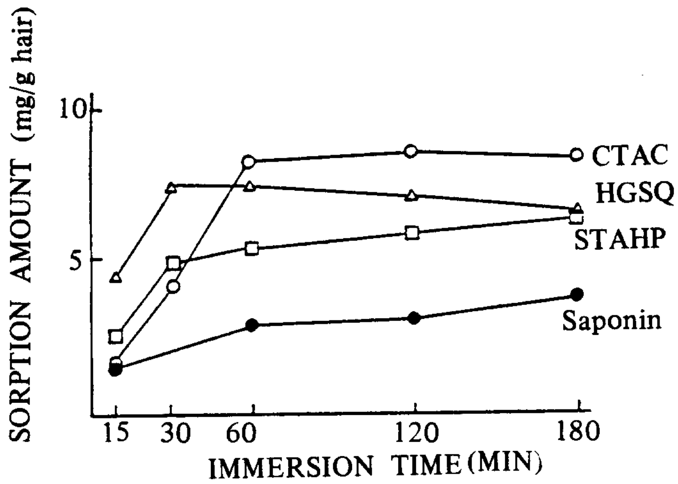


Figure 12. The effect of immersion time on sorption amount into virgin hair (conc'n 5%; temp. 20 ± 2°C; PH. 6.0 ± 0.1; RH. 60 ± 4%)

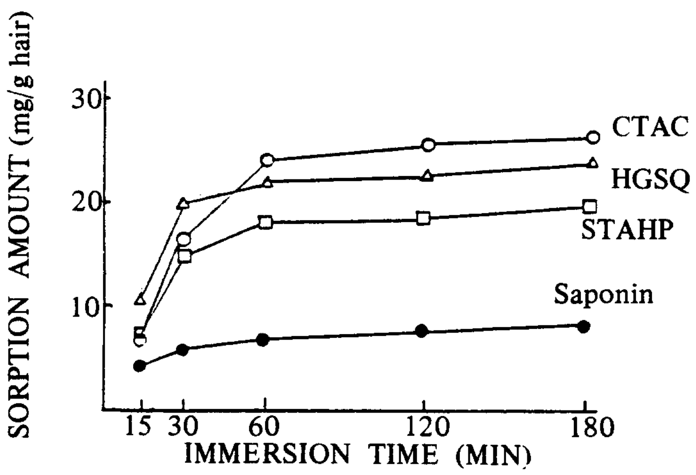


Figure 13. The effect of immersion time on sorption amount into bleached hair (conc' 5%; temp. 20 ± 2°C; PH. 6.0 ± 0.1; RH. 60 ± 4%)

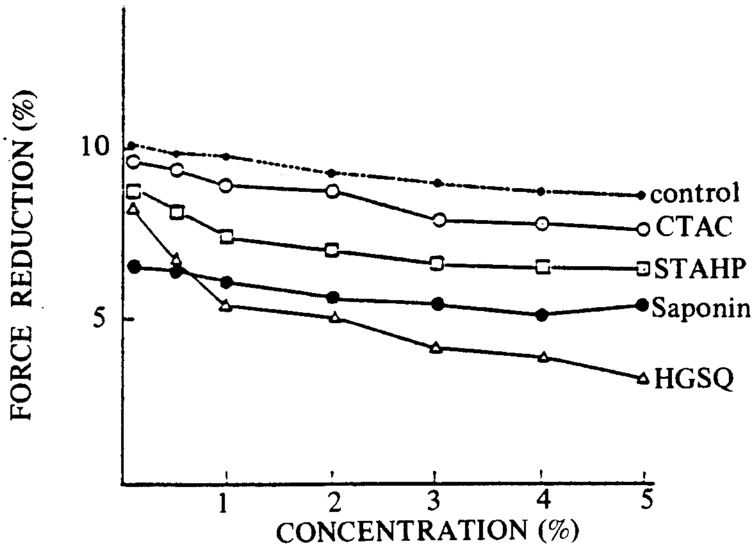


Figure 14. The effect of concentration on force reduction (%) of bleached hair (bleaching time 1hr; immersion time. 15hr; temp. 20 ± 2°C; RH. 60 ± 4%)

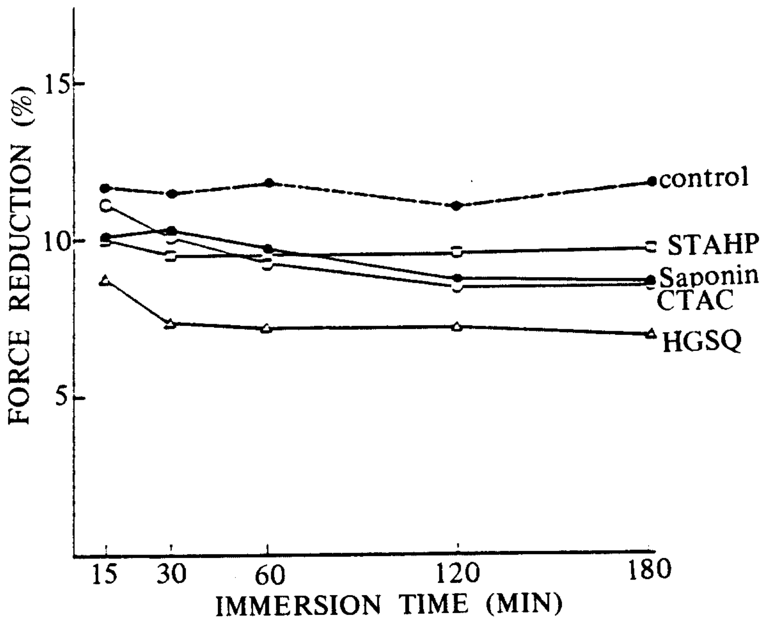


Figure 15. The effect of immersion time on force reduction (%) of bleached hair (bleaching time 1hr; conc'n 5%; temp. 20 ± 2°C; RH. 60 ± 4%)

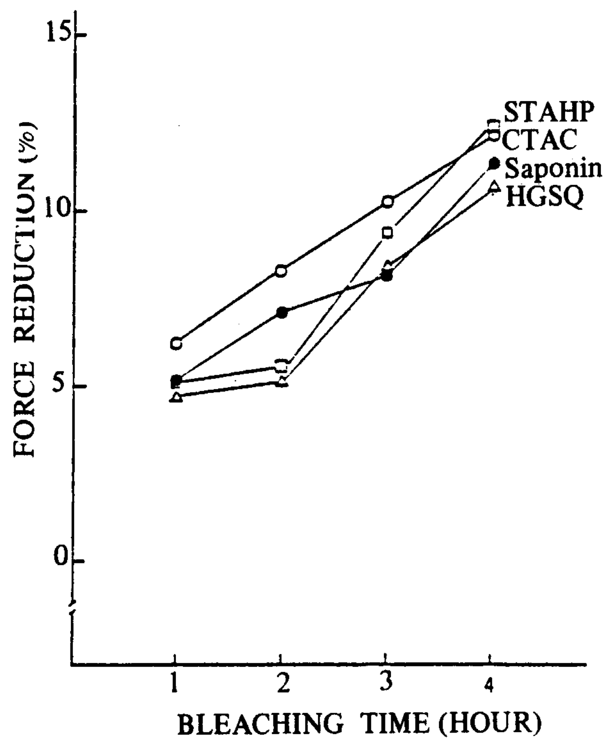


Figure 16. The effect of bleaching time on force reduction (%) of bleached hair (immersion time 15hr; conc'n 5%; temp. 20 ± 2°C; RH. 60 ± 4%)

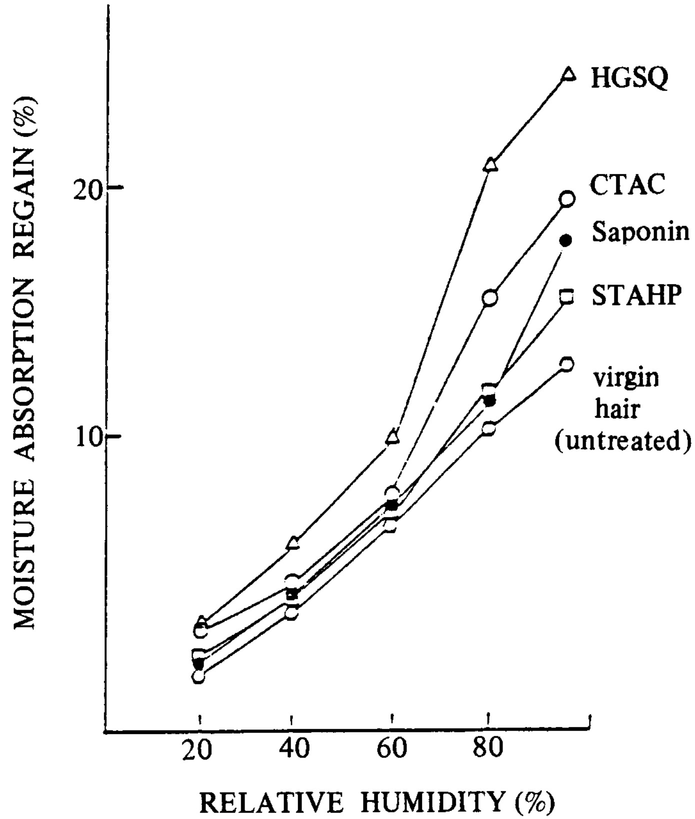


Figure 17. The moisture absorption regain isotherms of virgin hair treated with HGSQ, CTAC, saponin and STAHP (immersion time 15hr; con'c 0.5%; temp. 20 ± 2°C)

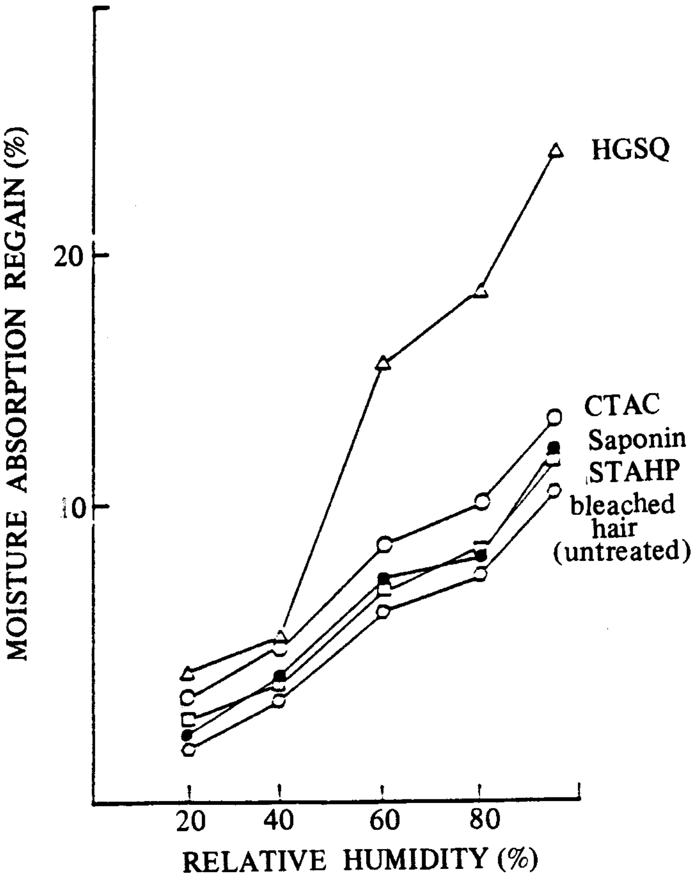


Figure 18. The moisture absorption regain isotherms of bleached hair treated with HGSQ, CTAC, saponin and STAHP (immersion time 15hr; conc'n 0.5%; temp. 20 ± 2°C)

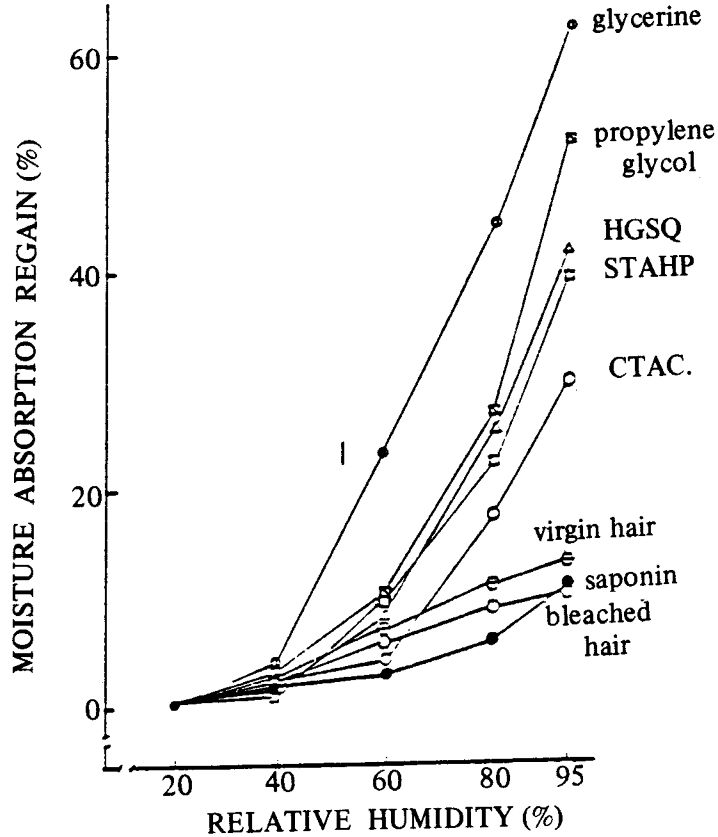


Figure 19. The moisture absorption regain isotherms of glycerine, propylene glycol, HGSQ, STAHP, CTAC, saponin, virgin hair and bleached hair (temp. 20 ± 2°C)