dye, 20 cc. of glacial acetic acid and 2 cc. of cyclopentadiene yielded a blue-black crystalline addition compound (0.16 g.). After two crystallizations from acetic acid, it melted at 176–177°.

Anal. Calcd. for $C_{17}H_{13}O_5N_4Br$: C, 47.11; H, 3.03. Found: C, 47.36; H, 3.13.

(8) **The Addition of Cyclopentadiene to Quinoneazine.**—One and one-tenth grams of quinoneazine dissolved in 15 cc. of benzene and cooled in an ice-bath was treated with 2 cc. of cyclopentadiene. At the end of two days, a small amount of the unreacted azine was filtered off and the filtrate evaporated to dryness under reduced pressure to give 0.7 g. of product. After twice dissolving in ethyl acetate and precipitating with petroleum ether, it was crystallized from ethyl acetate alone. Four crystallizations gave a yellow crystalline product melting at 149–150°. Analysis showed the addition of two molecules of cyclopentadiene.

Anal. Calcd. for $C_{22}H_{20}O_2N$: C, 76.69; H, 5.86. Found: C, 76.36; H, 6.12.

Summary

Cyclopentadiene adds to certain hydroxyazo compounds; a result which provides definite evidence that these substances may show quinoid character. The extent of addition is influenced by the acidity of the medium and its occurrence is not a general property of the *p*-hydroxyazo compounds.

MINNEAPOLIS, MINNESOTA RECEIVED OCTOBER 31, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Saponins and Sapogenins. III. The Sapogenins Obtained from Chlorogalum Pomeridianum

BY POE LIANG[1] AND C. R. NOLLER

Of the various plants used as fish poisons by the California Indians, the most important was a member of the lily family, *Chlorogalum pomeridianum* Kunth,[2] which is commonly known as California soap plant, or *amole*, the latter term being one commonly assigned by the Spanish-Californians and Mexicans to any of the various plants used as soap substitutes.

The only chemical investigation of this plant recorded in the literature is that of Trimble,[3] who reported a saponin content of 6.95% of the dry bulb. Our work shows that hydrolysis of the crude alcoholic extract of the bulbs yields two sapogenins which are especially interesting as they contain twenty-six carbon atoms and hence are related to the sapogenins obtained by the hydrolysis of the digitalis saponins, and by the hydrolysis of parillin, one of the sarsaparilla saponins,[4] instead of being triterpenoids like most sapogenins that have been carefully investigated.[5] One sapogenin has the empirical formula $C_{26}H_{42}O_4$,[6] and hence is isomeric with gitogenin which is obtained from gitonin, one of the digitalis saponins.[7] Like gitogenin it has two hydroxyl groups and two oxygen atoms which do not give reactions for any reactive type of oxygen linkage and hence must be assumed for the present to be of the ethylene oxide type. No color is obtained with tetranitromethane, indicating the absence of a double bond. The melting point of this sapogenin is 273–276° compared with 271–272° for gitogenin.[7] The compounds are not identical, however, because a marked depression was observed on taking a mixed melting point.[8] Moreover, the dibenzoate of the new sapogenin melts at 200–204° whereas gitogenin dibenzoate melts at 223–225°.[9] Since this sapogenin appears to be different from any previously reported, we have named it *chlorogenin.*

The other sapogenin isolated has the empirical formula $C_{26}H_{42}O_3$ and is isomeric with sarsasapogenin obtained from several varieties of smilax[10]

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[1] Research Fellow of the China Foundation for the Promotion of Education and Culture, 1933–34.

[2] Chestnut, *Contributions from the U. S. National Herbarium*, **7**, 319 (1902).

[3] Trimble, *Am. J. Pharm.*, **62**, 598 (1890).

[4] Jacobs and Simpson, *J. Biol. Chem.*, **105**, 501 (1934).

[5] Ruzicka and co-workers, *Helv. Chim. Acta*, **15**, 431 (1932).

[6] The difficulty of obtaining satisfactory combustion data on the sapogenins is well known. Our own analyses have all been by macrocombustion and the results for carbon do not agree well with the composition assigned to these sapogenins. In one instance we have had the sapogenin analyzed by a commercial microanalyst[15] and by a microanalyst[16] accustomed to the analysis of sapogenins. We consider it significant that the results of the latter[16] are in good agreement with the proposed formula. Of our own analyses we lay most stress on the saponification of the benzoates, which gave results readily reproducible with high accuracy and which support the formulas proposed.

[7] Windaus and Schneckenburger, *Ber.*, **46**, 2628 (1913).

[8] We are greatly indebted to Dr. W. A. Jacobs of the Rockefeller Institute for Medical Research for supplying us with pure samples of gitogenin, tigogenin and sarsasapogenin.

[9] Windaus and Brunken, *Z. physiol. Chem.*, **145**, 37 (1925).

[10] Van der Haar, *Rec. trav. chim.*, **48**, 726 (1929). It is of interest that *Smilax*, like *Chlorogalum*, is a member of the lily family.

and with tigogenin obtained from digitalis.[11] Like these compounds, it has one hydroxyl group, two oxygen atoms having unreactive linkages, and is saturated. Moreover, the melting point is very close to that of sarsasapogenin and of tigogenin. The melting point of the benzoate of sarsasapogenin,[12] however, is about 100° lower than that of this isomeric sapogenin, so that the two cannot be identical. This was confirmed by taking a mixed melting point of the two sapogenins,[8] when a marked lowering was observed. On the other hand, the melting point of the benzoate of the second sapogenin is about the same as that reported for tigogenin benzoate. Moreover, no depression was observed for the mixed melting points of either the sapogenins or their benzoates. In addition the specific rotations in pyridine are almost identical for the sapogenins and in fair agreement in the case of the benzoates. There seems little doubt, therefore, that the lower melting sapogenin is identical with tigogenin.

Since this work was submitted for publication Dr. A. F. Rogers, Professor of Mineralogy at Stanford University, has made a preliminary examination of crystals of tigogenin, of our lower melting sapogenin and of their benzoates, and has found that the two sapogenins are similar in appearance and optical properties, as are the two benzoates. Two of the three principle indices of refraction found for the sapogenins are $n_1 = 1.540 \pm 0.001$, $n_2 = 1.533 \pm 0.003$, and for the benzoates $n_1 = 1.560 \pm 0.001$, $n_2 = 1.520 \pm 0.001$.

Experimental

Isolation of the Sapogenins.—Quantities of the bulbs of *Chlorogalum pomeridianum* were collected between April and July in the low hills bordering the campus of Stanford University. The outer fibrous coat was removed and discarded and the inner portion ground in a food-chopper. As much of the juice as possible was removed in a cider press and strained through cloth. The pressed pulp was extracted exhaustively with hot methyl alcohol and the extract added to the expressed juice.

Numerous experiments on the hydrolysis of the extract indicated that the best results were obtained by adjusting the proportions of alcohol, water and concentrated hydrochloric acid to give a 50% aqueous methyl alcohol solution containing 5% hydrogen chloride, and refluxing for at least twenty-four hours. A dark brown precipitate formed which was thoroughly washed with water, dried in air, and extracted in large Soxhlet extractors with carbon tetrachloride. This extracted both sapogenins and practically none of the dark brown material. After removal of the carbon tetrachloride the mixed sapogenins were separated by alternate crystallization from methyl alcohol and isopropyl alcohol. It was found that the higher melting sapogenin is the less soluble in methyl alcohol, while the lower melting is the less soluble in isopropyl alcohol. The most satisfactory procedure was to dissolve the crude sapogenin in hot methyl alcohol, cool and filter, and wash the crystals with methyl alcohol. By concentrating and cooling the mother liquors a second and third crop of the higher melting crystals were obtained. The mother liquor was then evaporated to dryness, the residue dissolved in hot isopropyl alcohol and three crops of the lower melting crystals obtained. After evaporation of the mother liquors to dryness, the residue was again crystallized from methyl alcohol or combined with another batch of crude sapogenin. The higher melting fractions were then recrystallized from methyl alcohol and the lower melting from isopropyl alcohol until the melting points and rotations remained constant. Small amounts of decolorizing carbon were used from time to time to remove traces of color.

Chlorogenin.—After four or five recrystallizations of the higher melting fractions from methyl alcohol, the melting point remained constant at 273–276°;[13] $[\alpha]^{24}_{546}$ −52° in chloroform or isopropyl alcohol. When mixed with an equal amount of gitogenin,[8] m. p. 270–274°, a melting point of 250–258° was observed.

Anal. Calcd. for $C_{26}H_{40}O_2(OH)_2$: C, 74.54; H, 10.11; OH, 8.13; mol. wt., 418.3. Found: C, 73.5,[14] 75.03,[15] 75.23,[15] 74.53,[16] 74.87;[16] H, 9.95,[14] 9.97,[15] 9.84,[15] 10.24,[16] 10.14;[16] OH (by Zerewitinoff), 7.50, 7.32; mol. wt., 360–425 (ebullioscopic in isopropyl alcohol), 409, 425 (micro-Rast in camphor[15]).

Chlorogenin Dibenzoate.—A sample of pure chlorogenin was benzoylated by the procedure of Vesterberg and Westerlind.[17] After repeated recrystallization from a mixture of equal volumes of methyl alcohol and chloroform, the product melted at 200.5–204.5°; $[\alpha]^{26}_{546}$ +9.5° in chloroform.

Anal. Calcd. for $C_{26}H_{40}O_2(C_7H_5O_2)_2$: C, 76.62; H, 8.04; sap. equiv., 313.2; mol. wt., 626.4. Found: C, 76.03, 76.25; H, 7.94, 8.15; sap. equiv., 310–314 (min. and max. of 7 detns.); mol. wt., 524–578 (ebullioscopic in benzene).

Chlorogenin Di-*o*-bromobenzoate.—This compound was prepared from pure chlorogenin and *o*-bromobenzoyl chloride by the same procedure used for preparing the dibenzoate. After repeated recrystallization from a mixture of equal volumes of chloroform and 95% ethyl alcohol, it melted at 205–207°; $[\alpha]^{26}_{546}$ −9.5° in chloroform.

Anal. Calcd. for $C_{40}H_{48}O_6Br_2$: Br, 20.39. Found: Br, 20.66, 20.15, 20.42, 20.66, 20.60.

Tigogenin.—After four recrystallizations of the lower melting fractions from isopropyl alcohol, the melting point remained constant at 206.5–210° $[\alpha]^{26}_{546}$ −76.0° in chloroform or methyl alcohol; $[\alpha]^{26}_{546}$ −57.7° in pyridine; $[\alpha]^{26}_{D}$

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(11) Jacobs and Fleck, *J. Biol. Chem.*, **88**, 545 (1930).

(12) Kaufmann and Fuchs, *Ber.*, **56**, 2527 (1923).

(13) Practically all of the products obtained in this work had a rather wide melting point range. All products were repeatedly recrystallized, in some cases from several solvents, until no further change in the melting point or optical rotation took place.

(14) Average of six macro-combustions by the authors.

(15) Microanalyses by Dr. A. Schoeller, Berlin.

(16) Microanalyses by Dr. M. Furter, Zürich.

(17) Vesterberg and Westerlind, *Ann.*, **428**, 247 (1922).

−49.8° in pyridine. Jacobs and Fleck[11] reported the melting point of tigogenin as 203–204°; $[\alpha]^{25}_{D}$ −49° in pyridine. A mixture of a sample of m. p. 202–205° with approximately an equal amount of tigogenin,[8] m. p. 203–206°, melted at 202–206°. A mixture with sarsasapogenin,[8] m. p. 195–198°, melted at 182–191°.

Anal. Calcd. for $C_{26}H_{41}O_2(OH)$: C, 77.55; H, 10.51; OH, 4.22; mol. wt., 402.3. Found: C, 76.7, 76.1, 76.7, 76.2; H, 10.11, 10.32, 10.46, 10.41; OH (by Zerewitinoff), 3.71, 3.76; mol. wt., 388–423 (ebullioscopic in benzene).

Tigogenin Benzoate.—Benzoylated by the procedure of Vesterberg and Westerlind,[17] the sapogenin gave a monobenzoate which after repeated recrystallization from a mixture of equal volumes of methyl alcohol and chloroform melted at 220–224°. On further recrystallization from acetone the melting point rose to 230–233°; $[\alpha]^{22.5}_{546}$ −68° in chloroform; $[\alpha]^{25}_{546}$ −49.7° in pyridine; $[\alpha]^{24.5}_{D}$ −41.4° in pyridine.

Anal. Calcd. for $C_{26}H_{41}O_2(C_7H_5O_2)$: C, 78.20; H, 9.16; sap. equiv. and mol. wt., 506.4. Found: C, 77.20, 77.30; H, 9.14, 9.11; sap. equiv., 501–505 (min. and max. of 5 detns.); mol. wt., 485–547 (ebullioscopic in benzene).

Jacobs and Fleck[11] report the melting point of tigogenin benzoate as 224–225°; $[\alpha]^{26}_{D}$ −37° in pyridine. When a sample of tigogenin[8] was converted to the benzoate and purified by the above procedure it was found to melt at 230–233°. When mixed with the above benzoate of the same melting point, no depression was observed.

Tigogenin *o*-Bromobenzoate.—This was prepared from the sapogenin by the same procedure used to prepare chlorogenin di-*o*-bromobenzoate. Purification was effected by dissolving in the least possible amount of chloroform, evaporating about half of the solvent and adding twice the volume of 95% ethyl alcohol with rapid stirring. After three such treatments the product melted at 210–212°; $[\alpha]^{27}_{546}$ −56° (in chloroform).

Anal. Calcd. for $C_{33}H_{45}O_4Br$: Br, 13.55. Found: Br, 14.1, 13.93, 13.88.

Miscellaneous Experiments.—Neither the sapogenins nor their benzoates give a color with tetranitromethane in chloroform solution, indicating the absence of even unreactive double bonds. On treatment of the sapogenins with bromine in cold or hot alcoholic solution, no more bromine was absorbed than was found to react with the pure solvent and the sapogenins were recovered unchanged.

The absence of carboxyl, anhydride, ester, or lactone groups was shown by the fact that no alkali was consumed when either sapogenin was refluxed for thirty minutes with 0.4 *N* alcoholic potassium hydroxide solution. Moreover, after this treatment the sapogenins were recovered unchanged.

The same non-reactivity was shown on attempting to prepare oximes, semicarbazones, and 2,4-dinitrophenylhydrazones, indicating the absence of carbonyl groups.

The absence of methoxyl and ethoxyl groups was shown by Zeisel determinations.

Summary

Hydrolysis of the alcoholic extract of *Chlorogalum pomeridianum* gives two sapogenins. The higher melting has the formula $C_{26}H_{40}O_2(OH)_2$ and is isomeric with and closely resembles gitogenin, one of the digitalis sapogenins. The lower melting appears to be identical with tigogenin, $C_{26}H_{41}O_2(OH)$, another of the digitalis sapogenins.

STANFORD UNIV., CALIF. RECEIVED DECEMBER 6, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF LOUISVILLE]

Xenyl Esters and Ethers

BY C. C. VERNON, E. F. STRUSS, M. A. O'NEIL AND M. A. FORD

Certain xenyl[1] esters and ethers have been prepared in this Laboratory in connection with other studies on xenene and its derivatives.[2] Their physical constants and appearance are herein reported. In cases of the ethers, no evidence of ready rearrangement was found. The phosphate esters may have possibilities in celluloid manufacture, but were not found suitable for plasticizers, as was hoped.

Preparation of Sodium Xenate.—Xenols were allowed to react with such an excess of strong sodium hydroxide solution that the xenate formed crystallized on cooling from a sodium hydroxide solution, to prevent hydrolysis. If very pure sodium xenate was desired, xenol was dissolved in anhydrous benzene, and stirred while refluxing with metallic sodium. To prevent coating of the sodium, and to facilitate the removal of an excess, the sliced sodium was enclosed in a wire basket attached to the stirrer blades.

TABLE I

TRIXENYL ESTERS OF PHOSPHORIC ACID

Isomer		Ortho	Para
M. p., °C.		134.5	109
Crystals, fine white		Needles	Plates
Yield, %		60–61	43–46
Formula		$C_{36}H_{27}O_4P$	
Phosphorus, %	Calcd.	5.58	
	Found	5.68	5.88

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(1) Hale, THIS JOURNAL, **54**, 4458 (1932).

(2) Vernon, Rebernak and Ruwe, *ibid.*, **54**, 4456 (1932).