−49.8° in pyridine. Jacobs and Fleck[11] reported the melting point of tigogenin as 203–204°; $[\alpha]_D^{25}$ −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°; $[\alpha]_{546}^{22.5}$ −68° in chloroform; $[\alpha]_{546}^{25}$ −49.7° in pyridine; $[\alpha]_D^{24.5}$ −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°; $[\alpha]_D^{26}$ −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°; $[\alpha]_{546}^{27}$ −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	
Phosphorus, % 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).

TABLE II

XENYL ESTERS

Isomer			*p*-Butyl	*o*-Butyl	*p*-Ethanol	*o*-Ethanol
Crystal form			Large white opaque flakes	Heavy yellow liquid	White powder	Small white plates
M. p., °C			73	B. p., 137 (18 mm.)	107	68
Yield, %			88	30	88	60
Formula			$C_{16}H_{18}O$		$C_{14}H_{14}O_2$	
Analyses, %	Carbon	Calcd.	84.90	84.90	78.47	78.47
		Found	84.80	84.03	78.37	77.97
	Hydrogen	Calcd.	8.02	8.02	6.59	6.59
		Found	8.00	7.87	6.60	6.54

Trixenyl Esters of Phosphoric Acid.—Approximately 0.3 mole sodium xenate was allowed to react with 0.1 mole phosphorus oxytrichloride in anhydrous toluene solution. About half the solvent was removed by distillation, after completion of the reaction, and anhydrous ethyl alcohol added to aid precipitation of the ester, on cooling. Recrystallization was from anhydrous ethyl alcohol. For analysis, the esters were digested with concentrated sulfuric acid, and the resulting phosphoric acid determined by the common gravimetric methods.

Butyl and Hydroxyethyl Xenyl Ethers.—These were prepared by the method of Sowa, Hinton and Nieuwland,[3] because previous runs with sodium xenate and alkyl halides under anhydrous conditions gave small yields.

Summary

The butyl and hydroxyethyl ethers and the complete phosphate esters of *o*- and *p*-xenols have been prepared and some of their physical characteristics described.

[3] Sowa, Hinton and Nieuwland, THIS JOURNAL, **54**, 2019 (1932).

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[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. XI. The Nature of Lignite Humic Acid and of the So-called "Humic Acid" from Sucrose[1,2]

BY MARK PLUNGUIAN AND HAROLD HIBBERT

Introduction

Natural humic acids have been defined[3,4] as those dark brown amorphous substances, resulting from the natural decomposition of plant residues, which are soluble in dilute alkali and which may be precipitated from these solutions by mineral acids.

Synthetic humic acids may be defined as the dark-brown, alkali-soluble amorphous substances obtained in the laboratory by the vigorous action of mineral acids and oxidizing agents on carbohydrates,[5] proteins,[6] phenols,[7] furans[8] and solid hydrocarbons.[9]

For one hundred years after Braconnot[10] first described the preparation of synthetic humic acids from carbohydrates, the identity of these acids with, or their close relationship to, the naturally occurring humic acids was quite generally assumed to be true in spite of the complete lack of chemical evidence for such belief. The ease of formation of these synthetic humic acids from carbohydrates in the laboratory led to the other tacit assumption that the origin of the natural humic acids should be looked for in the carbohydrate part of the decaying plant material and that wood cellulose chiefly was the precursor of natural humic acid. This assumption remained unchallenged until Fischer and Schrader[11] in 1921 put forward their "lignin theory" of the origin of humic acid and of coal. According to this theory the cellulose is largely destroyed by bacterial decomposition, the lignin fraction of the plant substance being more resistant to decay. The nu-

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[1] This work was presented at the Cleveland, Ohio, meeting of the American Chemical Society, September, 1934.

[2] Abstracted from a thesis presented by Mark Plunguian to McGill University in partial fulfilment of the requirements for the Ph.D. degree, October, 1934.

[3] S. Odén, *Kolloidchem. Beihefte*, II, 75–260 (1919).

[4] W. Fuchs, *Kolloid-Z.*, **52**, 248, 350; **53**, 124 (1930).

[5] (a) M. Conrad and M. Guthzeit, *Ber.*, **19**, 2844 (1886); (b) W. B. Bottomley, *Biochem. J.*, **9**, 260 (1915); (c) R. S. Hilpert and E. Littman, *Ber.*, **67**, 1551 (1934).

[6] R. A. Gortner and E. R. Norris, THIS JOURNAL, **45**, 550 (1923).

[7] Wm. Eller and K. Koch, *Ber.*, **53B**, 1469 (1920).

[8] J. Marcusson, *ibid.*, **54B**, 542 (1921).

[9] N. A. Orlov and V. V. Tischenko, *J. Applied Chem.* (*U. S. S. R.*), **6**, 112 (1933).

[10] H. Braconnot, *Ann. chim. phys.*, **12**, 172 (1819).

[11] F. Fischer and H. Schrader, *Brennstoff-Chem.*, **2**, 27 (1921).