To the ester (50 g.) was added 5 g. of catalyst and the mixture placed under a pressure of 1840 lb. of hydrogen. The temperature was then slowly raised. Hydrogenation of the double bond took place at a pressure of 2550 lb. and a temperature of 146°. If the hydrogenation were interrupted at this point, an approximately quantitative yield (98%) of ethyl 2,3-dimethoxydihydrocinnamate, b. p. 174–176° at 13 mm., could be obtained.

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.6; H, 7.57. Found: C, 65.6; H, 7.55.

At a pressure of 2680 lb. and a temperature of 224°, further hydrogen was consumed and the principal product weighing 34 g. (86%), distilled at 160–165° at 13 mm. The product failed to crystallize. For identification, a phenylurethan was prepared. This compound melted at 62.7–63.2° after crystallization from petroleum ether.

Anal. Calcd. for $C_{18}H_{21}O_4N$: C, 68.6; H, 6.70. Found: C, 68.4; H, 6.67.

2,3-Dimethoxydihydrocinnamyl Chloride and Bromide.—The halides corresponding to 2,3-dimethoxydihydrocinnamyl alcohol were prepared by the action of thionyl chloride or hydrogen chloride, and hydrogen bromide or 48% hydrobromic acid. They were separated and subjected to a variety of demethylation procedures without further identification. The dihydric phenols could not be isolated; resins were frequent products. Nor was it found possible to prepare by demethylation the 2,3-dihydroxybenzyl halides. However, during sealed tube demethylations in the presence of concentrated hydrobromic and hydriodic acids, catechol itself was formed and isolated in yields up to 18% from these 3-substituted catechol ethers. This has also been encountered during acid demethylation of 2,3-dimethoxy-*n*-pentadecylbenzene,[1] and by Haworth[12] during the acid demethylations of 3- and 4-substituted catechol ethers. Lability of alkyl substituents in the veratrole molecule under these conditions is thus indicated.

Acknowledgment.—I am indebted to Dr. Arthur T. Ness and to Mr. Charles A. Kinser for the microchemical analyses.

[12] Haworth and Woodcock, *J. Chem. Soc.*, 999 (1947).

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New Sources for Sapogenins

BY RUSSELL E. MARKER, R. B. WAGNER, PAUL R. ULSHAFER, EMERSON L. WITTBECKER, DALE P. J. GOLDSMITH AND CLARENCE H. RUOF

The isolations of various steroidal sapogenins from many plant sources have been reported previously from this Laboratory.[1,2,3] The results of our studies on additional plants are now summarized.

Among the new sources for steroidal sapogenins is the seed of *Trigonella Foenum-graecum* L. (Foenugreek). For their isolation 460 kg. of seeds were processed. There has been isolated from the mother liquor after the separation of diosgenin (yield, about 1.0 g./kg. dry seed),[4] two more sapogenins, namely, tigogenin (trace) and gitogenin (yield, 0.1 g./kg. dry seed). The last two sapogenins have occurred jointly in other plants, namely, *Yucca Whipplei* Torr. subsps. *intermedia*, *Agave gracilipes* Trel. and *Agave Schottii* Engelm. However, this is the first and single case of the occurrence of all three in the same plant. The significance of this finding has been discussed.[3b]

Lilagenin has been isolated from the sapogenin fraction of *Lilium rubrum magnificum*.[5] In addition, a small amount of yuccagenin was found.

In our preliminary paper,[3a] we erroneously reported *Samuela Faxoniana* Trel. to be a source for smilagenin. Actually, it is a new source for sarsasapogenin.

Other new sources are listed in the accompanying tables.

TABLE I

PLANTS CONTAINING DIOSGENIN AND KRYPTOGENIN

Plant	Location	Yield g. per kg. (dry) plant Dios.	Krypt.
Balanites aegyptica Wall.	Southern Mexico	5.0	1.0
Dioscorea floridiana Bartlett	Southern Georiga	1.7	...
Dioscorea glauca Muhl.	North Carolina,	1.0	...
Trillium Catesbaei Ell.	North Carolina	...	0.1
Trillium cernum L.	North Carolina	...	1.0
Trillium decumbens Harbison	North Carolina	...	0.5
Trillium declinatum Gleason	Tennessee	5.0	1.0
Trillium erectum L.	North Carolina	3.0	0.2
Trillium Hugeri Small	North Carolina	3.0	...
Trillium ludovicianum Harbison	Georgia	5.0	...
Trillium recurvatum Beck	Mississippi	4.0	Trace
Trillium simile Gleason	North Carolina	4.0	...
Trillium stamineum Harbison	Georgia	...	0.8
Trillium Vaseyi Harbison	North Carolina	0.4	...
Trillium viride Beck	North Carolina	...	0.5

PLANTS CONTAINING SITOSTEROL

Plant	Location	Yield, g. per kg. dry plant
Areca Catechu L.	Commercial	Trace
Arisaema triphyllum Schott	Commercial	0.5
Jatrorrhiza palmata Miers	Commercial	Trace
Smilacina racemosa Desf.	State College, Pa.	Trace
Zanthorhiza apiifolia L'Hérit	Commercial	Trace

The identities of the above compounds were established by analyses of the genins and their acetates along with melting point and mixed melting point determinations on both. Generalized isolation procedures have been reported.[3b]

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[1] Marker, Turner and Ulshafer, THIS JOURNAL, **62**, 2542 (1940).

[2] Marker, Wagner and Ulshafer, *ibid.*, **64**, 1283 (1942).

[3] (a) Marker, Wagner, Ulshafer, Wittbecker, Goldsmith and Ruof, *ibid.*, **65**, 1199 (1943); (b) **69**, 2167 (1947); (c) for supplementary tables, order Document 2384 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting 50¢ for microfilm or $2.10 for photocopies.

[4] Marker, Wagner, Ulshafer, Goldsmith and Ruof, *ibid.*, **65**, 1247 (1943).

[5] Marker, Turner, Shabica, Jones, Krueger and Surmatis, *ibid.*, **62**, 2620 (1940).

[6] Original manuscript received June 26, 1944.

The Use of a Fluorescent Adsorbent for the Chromatography of Colorless Compounds

BY JOHN W. SEASE

When colorless compounds which absorb ultraviolet light are chromatographed on a fluorescent

TABLE I

SEPARATIONS OF PAIRS OF COMPOUNDS ON SILICA COLUMNS MADE FLUORESCENT BY ADDITION OF FLUORESCENT ZINC SULFIDE

Compound A	Mg.	Compound B	Mg.	Petroleum ether developer, ml.	Zones,[a] mm. I	II	III	IV	V
Azoxybenzene	10	Nitrobenzene	10	100	22	20	20	20	60
p-Nitrobenzyl bromide	18.2	Nitrobenzene	10	100	20	10	40	20	50
Salicylaldehyde	2.6	Nitrobenzene	6	50	50	15	10	10	20
Cinnamaldehyde	4.9	Salicylaldehyde	2.6	40	0	5	40	10	35
Cinnamaldehyde	4.2	Azoxybenzene	8.0	50	15	5	20	30	30
p-Nitrobenzyl bromide	14.6	Azoxybenzene	8.0	65	45	20	5	30	5
Cinnamaldehyde	4.9	*p*-Nitrobenzyl bromide	14.6	200	0	2	45	15	80
p-Nitrobenzyl bromide	10.9	Salicylaldehyde	5.1	160	35	15	5	10	80
Xanthone	3.6	*p*-Nitrobenzyl bromide	10.9	80	0	5	10	8	120
Nitrobenzene	6.0	Iodoform	4.6	25	15	10	55	30	35

[a] Each chromatogram is described in terms of the following zones, whose thicknesses in mm. are given by the numbers under the corresponding Roman numerals: I, fluorescent (empty) section; II, shadow (upper zone, Compound A); III, fluorescent (empty) section; IV, shadow (lower zone, Compound B); V, fluorescent (empty) section.

adsorbent, the fluorescence is found, under appropriate conditions, to decrease in those regions of the column where the zones of colorless, non-fluorescing adsorbate are located. Adsorbents with fluorescent and adsorptive properties suitable for this work may be conveniently prepared by mixing a finely powdered inorganic fluorescent material with a standard chromatographic adsorbent, such as alumina or silica gel. With the aid of such a mixture it has been found possible to follow visually the development of chromatograms of some colorless, non-fluorescing substances as readily as in the case of fluorescent compounds.[1]

A series of experiments using silica gel with which had been mixed a small amount of fluorescent zinc sulfide (no. 62)[2] led to the following adsorption sequence, the compounds being listed in order of decreasing adsorption affinity when developed with petroleum ether

{Cinnamaldehyde[3]
{Xanthone[3]
p-Nitrobenzyl bromide
{Salicylaldehyde[3]
{Azoxybenzene[3]
Nitrobenzene
Iodoform

Details of the individual chromatograms are given in Table I.

Both an argon glow lamp[4a] and an incandescent ultraviolet lamp[4b] were found to be suitable light sources for practical work.[5]

Three different zinc sulfides were tested in preliminary experiments.[2] All three gave approximately equivalent results, although yellow fluorescence was found to be preferable since both available ultraviolet sources had an appreciable output of violet or blue light.

Qualitative tests were carried out with the optical system of a Beckman Spectrophotometer as an ultraviolet source in order to learn what wave lengths were effective in exciting the fluorescence. All three zinc sulfides were found to be sensitive to approximately the same wave lengths. For practical purposes the upper and lower limits for the exciting radiation were found to be approximately 390 and 330 mμ, respectively. This applies to the mixture of zinc sulfide and silica (2.5% no. 62 zinc sulfide) as used in these experiments, *i. e.*, packed inside a standard Pyrex chromatographic tube[6] and wet with petroleum ether.

The use of other inorganic fluorescent materials which are sensitive to wave lengths below 330 mμ is being investigated at the present time.

Experimental

A solution in 5–10 ml. of petroleum ether (Skellysolve B, b. p. 60–70°) of the two substances to be separated was poured on a column (1.8 cm. diameter, 9–15 cm. long) of silicic acid (Eimer and Amend, C. P., mixed with 2.5% of no. 62 fluorescent zinc sulfide[2]). Movement of the zones on development with additional petroleum ether was observed by illuminating the column in a darkened room with ultraviolet light.[4a,b]

At the conclusion of development the column was extruded and each portion of adsorbent containing a shadowed zone was cut out. Elution of each zone with 30–40

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[1] After submission of this manuscript for publication the author learned of a prior publication by H. Brockmann and F. Volpers (*Ber.* **80**, 77 (1947)) in which the application of fluorescent adsorbents to chromatography of colorless compounds is described. Their adsorbents were prepared by adsorbing morin, diphenylfluorindinesulfonic acid, or salicylic acid on alumina, by adsorbing berberine on silicic acid, or by adsorbing morin or diphenylfluorindinesulfonic acid on magnesia or calcium carbonate. The limits for exciting radiation were found to be 250–400 mμ.

[2] Three fluorescent zinc sulfides were obtained through the courtesy of the Patterson Screen Division of E. I. du Pont de Nemours and Co., Inc., Towanda, Pa.: No. 16, Blue fluorescence, no afterglow; No. 50, Yellow fluorescence, afterglow; No. 62, Yellow fluorescence, no afterglow.

[3] Bracketed pairs could not be separated completely (*i. e.*, with an empty, fluorescing interspace between the shadowed zones) when developed with petrolum ether on columns of 15 cm. or less in length and therefore are not included in Table I. Partial separations were obtained, however, so that the relative adsorption affinities could be determined.

[4] (a) Cenco No. 71370, complete with ultraviolet filter; (b) Purple X, General Electric Co.; no filter was used.

[5] The broad spectral band furnished by such light sources is undesirable. A considerable increase in sensitivity of detection would be expected if there were available a much narrower spectral band whose average wave length approximated that of the spectral absorption maximum of the compound being observed on the column.

[6] Manufactured by Scientific Glass Apparatus Co., Bloomfield, N. J.

ml. of 96% ethanol gave a solution whose qualitative and quantitative composition could easily be determined on a Beckman Spectrophotometer.

The adsorbent can be recovered by placing in a chromatographic tube, washing with enough 96% ethanol to wet the entire column, then washing with three times this volume of petroleum ether, and finally drying in the air at room temperature. Silica–zinc sulfide mixture so recovered showed slightly weaker adsorptive properties than fresh adsorbent, but was its equivalent for all practical purposes. Both fresh and recovered mixtures were used in this work.

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Osmotic and Activity Coefficients of Lithium Bromide and Calcium Bromide Solutions

BY R. A. ROBINSON AND H. J. McCOACH

The osmotic and activity coefficients of lithium chloride and calcium chloride solutions have been determined recently[1,2] up to the highest concentrations. Similar measurements on the bromides have now been made to extend the concentration range beyond that of earlier measurements.[3,4]

Isopiestic determinations were made using platinum dishes as it has been found that some corrosion of silver dishes occurs with concentrated bromide solutions. Calcium chloride and sulfuric acid were used as reference electrolytes. The molalities of pairs of solutions of equal vapor pressure are given in Table I. From these measurements the osmotic and activity coefficients given in Table II were evaluated. This table contains values at low concentrations, the earlier data having been recalculated to conform with more recent reference data.[5]

TABLE I

MOLALITIES OF ISOPIESTIC SOLUTIONS AT 25°

LiBr	$CaCl_2$	LiBr	$CaCl_2$	LiBr	$CaCl_2$	LiBr	$CaCl_2$
4.837	3.110	5.937	3.756	6.913	4.345	7.942	4.984
9.388	5.980	10.12	6.553	11.02	7.426	11.87	8.342

LiBr	H_2SO_4	LiBr	H_2SO_4	LiBr	H_2SO_4	LiBr	H_2SO_4
11.95	12.85	13.61	15.29	14.33	16.32	15.46	17.88
16.14	18.80	16.47	19.20	16.58	19.35	17.09	20.04
18.39	21.64	18.99	22.35	19.85	23.21		

$CaBr_2$	$CaCl_2$	$CaBr_2$	$CaCl_2$	$CaBr_2$	$CaCl_2$	$CaBr_2$	$CaCl_2$
1.422	1.524	1.766	1.897	2.140	2.309	2.152	2.321
2.554	2.764	2.584	2.801	2.791	3.026	3.116	3.387
3.565	3.888	3.785	4.158	3.922	4.312	4.435	4.965
5.144	5.952	5.595	6.655	5.726	6.893	5.984	7.470
6.170	7.831	6.286	8.067	6.406	8.375	6.583	8.730
6.630	8.838	6.863	9.498	6.965	9.815	7.216	10.41

$CaBr_2$	H_2SO_4	$CaBr_2$	H_2SO_4	$CaBr_2$	H_2SO_4	$CaBr_2$	H_2SO_4
7.636	16.10	7.922	16.81	8.406	17.97	9.210	19.61

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF LITHIUM AND CALCIUM BROMIDE AT 25°

	LiBr		$CaBr_2$	
m	φ	γ	φ	γ
0.1	0.943	0.796	0.863	0.532
.2	.944	.766	.878	.492
.3	.952	.756	.900	.482
.4	.960	.752	.927	.483
.5	.970	.753	.958	.491
.6	.981	.758	.990	.505
.7	.993	.767	1.022	.522
.8	1.007	.777	1.057	.543
.9	1.021	.789	1.093	.568
1.0	1.035	.803	1.131	.597
1.2	1.067	.837	1.207	.665
1.4	1.098	.874	1.286	.747
1.6	1.130	.917	1.370	.848
1.8	1.163	.964	1.455	.970
2.0	1.196	1.015	1.547	1.121
2.5	1.278	1.161	1.790	1.657
3.0	1.364	1.341	2.048	2.54
3.5	1.467	1.584	2.297	3.89
4.0	1.578	1.897	2.584	6.28
4.5	1.687	2.28	2.908	10.66
5.0	1.793	2.74	3.239	18.47
6.0	1.989	3.92	3.880	55.8
7.0	2.206	5.76	4.463	163.0
8.0	2.432	8.61	4.809	375
9.0	2.656	12.92	4.969	696
10.0	2.902	19.92	...	.....
11.0	3.150	31.0	...	.....
12.0	3.356	46.3	...	.....
13.0	3.581	70.6	...	.....
14.0	3.776	104.7	...	.....
15.0	3.912	146.0	...	.....
16.0	4.025	198.0	...	.....
17.0	4.110	260	...	.....
18.0	4.173	331	...	.....
19.0	4.216	411	...	.....
20.0	4.217	485	...	.....

CHEMISTRY DEPARTMENT
AUCKLAND UNIVERSITY COLLEGE
NEW ZEALAND
RECEIVED JUNE 26, 1947

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(1) R. A. Robinson, *Trans. Faraday Soc.*, **41**, 756 (1945).

(2) R. H. Stokes, *ibid.*, **41**, 637 (1945).

(3) R. A. Robinson, THIS JOURNAL, **57**, 1161 (1935).

(4) R. A. Robinson, *Trans. Faraday Soc.*, **38**, 445 (1942).

(5) (a) S. Shankman and A. R. Gordon, THIS JOURNAL, **61**, 2370 (1939); (b) R. H. Stokes and B. J. Levien, *ibid.*, **68**, 333 (1946); (c) R. H. Stokes, *ibid.*, **69**, 1291 (1947).

A Claisen Condensation by a Primary Grignard Reagent

BY S. B. SOLOWAY AND F. B. LAFORGE

The abnormal reactions of the Grignard reagents have been frequently reported in the literature. In the majority of such reactions the Grignard reagent has been prepared from either a secondary or a tertiary halide. Recently the Claisen condensation of esters by the agency of *t*-butylmagnesium chloride has been reported.[1] In this note we describe a mixed ketone–ester condensation by means of a Grignard reagent prepared from a primary halide.

The reaction between ethyl levulinate and the Grignard reagent is known to give low yields of

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(1) Zook, McAleer and Horwin, *ibid.*, **68**, 2404 (1946).