the reason that the other eight lines and vibrations were satisfactorily correlated. The large difference between 1538 and the frequency 830 of the out-of-plane vibration of the nitrate ion was pointed out.

M. Freymann and R. Freymann[2] recently reported a moderately strong double band 771 and 792 cm.$^{-1}$ in the infrared spectrum of nitric acid vapor corresponding to a weak line 768 in the Raman spectrum of Simon and Hoeppner.[3] The correlation of this band with the out-of-plane vibration, mentioned but not finally adopted by Freymann and Freymann, is strongly supported by the fact that 1538 cannot be correlated with any other vibration. Obviously the Raman line 1538 represents not the fundamental but the first harmonic of the out-of-plane vibration.

With this change the earlier analysis of the vibration spectrum appears to represent all known data in a satisfactory way. Some of our conclusions coincide with earlier results of Mathieu and Massignon.[4]

The somewhat unusual intensity of 1538 can hardly be explained by accidental degeneracy with vibration 4 (1669 cm.$^{-1}$) since the selection rules for C_{2v} do not permit this resonance. A slight interaction with 1301 cm.$^{-1}$ appears to be possible.

The author is obliged to Professor G. Herzberg for a helpful discussion.

[2] M. Freymann and R. Freymann, *Compt. rend.*, **222**, 1339 (1946).

[3] A. Simon and H. Hoeppner, *Kolloid-Z.*, **86**, 8 (1939).

[4] J. P. Mathieu and D. Massignon, *Ann. phys.*, **16**, 5 (1941).

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIFORNIA

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The Allergenic Principles of Poison Ivy. VI. Note on the Synthesis of 3-Substituted Catechols[1,1a]

BY HOWARD S. MASON

In this study, 3-bromocatechol and its diphenylmethylene ether have been synthesized to provide the nuclear fragment for the synthesis of unsaturated allergens related to the catechols of poison ivy. 2,3-Dimethoxydihydrocinnamyl halides have also been prepared; these substances proved refractory toward demethylation.

Experimental

2,3-Dimethoxybromobenzene.—2,3-Dimethoxybenzoic acid was prepared from 2,3-dimethoxybenzaldehyde[2] in 84% yield by permanganate oxidation.[3] This substance was converted to 2,3-dimethoxybenzamide in 88% yield.[4] The amide furnished 2,3-dimethoxyaniline in 83% yield by adapting to the synthesis the procedure for the Hofmann rearrangement worked out by Buck and Ide.[5] Bigelow's procedure for the Sandmeyer replacement[6] was then modified for the preparation of 2,3-dimethoxybromobenzene; this resulted in a considerably improved yield. To a cuprous bromide solution prepared in 275 ml. of water was added a solution of 2,3-dimethoxybenzenediazonium sulfate prepared from 52 g. of 2,3-dimethoxyaniline hydrochloride. The addition required two hours; the reaction mixture was kept boiling vigorously and the product steam-distilled out as formed. The principal product distilled at 111–113° at 9 mm. and weighed 53 g. (89%). After cooling overnight, the compound solidified. It then melted at 22.7–23.2°. Simonsen and Rau[7] report a boiling point of 114° at 5 mm. Their product did not crystallize.

Anal. Calcd. for $C_8H_9O_2Br$: C, 44.3; H, 4.18. Found: C, 44.5; H, 4.45.

The compound was further identified by the preparation of 2,3-dimethoxy-5-nitrobromobenzene, which melted at 112.3–112.7°. The reported melting point is 112–113°.[7]

3-Bromocatechol.—2,3-Dimethoxybromobenzene was most efficiently demethylated by treating this ether with aluminum trichloride in chlorobenzene.[8] To 50 ml. of dry chlorobenzene was added 5.0 g. of 2,3-dimethoxybromobenzene and 5.0 g. of anhydrous aluminum trichloride. The mixture was refluxed for three and one-half hours, then poured into water and extracted with ether (400 ml.). The ether solution was dried and the solvent evaporated; the residue was then distilled. The principal fraction was an oil which boiled at 118–120° at 9 mm. After crystallization from isoöctane–pentane, long silky needles melting at 40.5–41.5° were obtained. The product weighed 3.5 g. (80%).

Anal. Calcd. for $C_6H_5O_2Br$: C, 38.1; H, 2.68. Found: C, 38.3; H, 2.71.

2,3-Diacetoxybromobenzene.—This substance crystallized from aqueous methanol in needles melting at 83–84°.

Anal. Calcd. for $C_{10}H_9O_4Br$: C, 44.0; H, 3.32. Found: C, 44.1; H, 3.37.

3-Bromocatechol Diphenylmethylene Ether.—3-Bromocatechol (19 g.) and dichlorodiphenylmethane (24 g.) were mixed with a little dry benzene and warmed on a hot-plate until hydrogen chloride no longer evolved. The product crystallized from methanol in white tablets melting at 75.5–76°; the yield was 97%.

Anal. Calcd. for $C_{19}H_{13}O_2Br$: C, 64.6; H, 3.71. Found: C, 64.6; H, 3.68.

Ethyl 2,3-Dimethoxycinnamate.—The procedure for the Claisen reaction developed by Marvel and King[9] was adapted to this synthesis. The principal product from 83 g. of 2,3-dimethoxybenzaldehyde distilled at 195–197° at 15 mm. and weighed 101 g. (86%). For identification, this ester was hydrolyzed to 2,3-dimethoxycinnamic acid, m. p. 179–180°; this m. p. has previously been reported to be 181°.[10]

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.5; H, 5.77. Found: C, 63.6; H, 5.79.

Ethyl 2,3-Dimethoxydihydrocinnamate and 2,3-Dimethoxydihydrocinnamyl Alcohol.—Ethyl 2,3-dimethoxycinnamate was hydrogenated over copper chromite catalyst according to the general directions of Folkers and Adkins.[11]

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[1] Article not copyrighted. For the fifth paper in this series, see Mason, THIS JOURNAL, **67**, 1538 (1945).

[1a] The author regrets that the work of Keil, Wasserman and Dawson, *J. Exp. Med.*, **80**, 275 (1944), was not mentioned in the last article.

[2] The starting material was generously furnished by the Monsanto Chemical Company.

[3] Perkin and Robinson, *J. Chem. Soc.*, **105**, 2383 (1914).

[4] Mauthner, *J. prakt. Chem.*, **149**, 328 (1937).

[5] Buck and Ide, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, editor, John Wiley and Sons, Inc., London, 1943, p. 44.

[6] Bigelow, "Organic Syntheses," 2nd ed., Coll. Vol. I, H. Gilman and A. H. Blatt, editors, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 136.

[7] Simonsen and Rau, *J. Chem. Soc.*, **113**, 785 (1918).

[8] Dawson, Wasserman and Keil, THIS JOURNAL, **68**, 534 (1946).

[9] Marvel and King, "Organic Syntheses," 2nd ed., Coll. Vol. I. H. Gilman and A. H. Blatt, editors, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 252.

[10] Chakravarti, *J. Indian Chem. Soc.*, **6**, 207 (1929).

[11] Folkers and Adkins, THIS JOURNAL, **54**, 1145 (1932).

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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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

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