Anal. Calcd for $C_{14}H_5F_5$: F, 35.42; mol wt, 268. Found: F, 36.43; mol wt, 260 (osmometry in benzene).

Preparation of Bis(pentafluorophenyl)acetylene (I).—α-2,3,4,5,6-Pentafluorobenzoyl-2,3,4,5,6-pentafluorobenzylidenetriphenylphosphorane (1.0 g, 0.00157 mole) was heated at 310° (10 mm) as described above to give 0.53 g (95%) of a flocculent white precipitate, mp 122–123° (sublimation). The infrared spectrum of this material revealed the absence of C-C triple-bond absorption in the 2200-cm^{-1} region, as expected. The product failed to show any pmr absorption.

Anal. Calcd for $C_{14}F_{10}$: F, 53.04; mol wt, 358. Found: F, 52.95; mol wt, 354 (osmometry in benzene).

Preparation of Copper Phenylacetylide.—Copper phenylacetylide was prepared by a method described previously.[2]

Preparation of II.—To a 250-ml, three-necked flask, equipped with a nitrogen inlet, a reflux condenser connected to a mercury trap, and a magnetic stirring bar, were added 3.6 g (0.022 mole) of cuprous phenylacetylide and 80 ml of dimethylformamide (DMF). The flask and contents were thoroughly flushed with nitrogen with stirring. Under nitrogen, 6.5 g (0.023 mole) of iodopentafluorobenzene in 20 ml of DMF were added. The contents were stirred and warmed in an oil bath at 140° for 15 hr. The reaction mixture turned dark. The mixture was cooled filtered, placed on a rotatory evaporator, and concentrated to dryness. The black tarlike material was dissolved in 95% ethanol and crystals formed after the flask was stored in a refrigerator. The first recrystallization from ethanol gave 1.65 g (20%) of the crude acetylene. The infrared spectrum was identical with that of an authentic sample of II. Optimum conditions for the synthesis of the acetylene were not worked out. It was found, however, that longer reaction times and higher temperatures produced a more impure product.

Preparation of Hexaarylbenzenes.—Tetraphenylcyclopentadienone (0.5 g, 0.0013 mole) and the appropriate acetylene (for II, 0.75 g, 0.0028 mole; for I, 1 g, 0.0028 mole) were placed in a 25 × 150 mm test tube and heated with the flame from a microburner. The excess acetylene was removed with a cold finger. The residue, upon cooling, was recrystallized from diphenyl ether to yield off-white crystals. The melting points of the products could not be determined since they were above 300°. The yield for both hexaarylbenzenes was 60%. The infrared spectra were consistent with polysubstituted benzenes and showed no carbonyl stretching band in either case and no C≡C band in the case of the unsymmetrical acetylene.

Anal. Calcd for $C_{42}H_{25}F_5$: C, 80.75; H, 4.03. Found: C, 80.83; H, 4.06. Calcd for $C_{42}H_{20}F_{10}$: C, 70.59; H, 2.82. Found: C, 70.98; H, 2.91.

Registry No.—I, 13557-43-2; II, 13509-88-1; benzyltriphenylphosphonium bromide, 1449-46-3; 2,3,4,5,6-pentafluorobenzyl bromide, 1765-40-8; 2,3,4,5,6-pentafluorobenzyltriphenylphosphonium bromide, 13509-91-6; pentafluorobenzoyl chloride, 653-35-0; α-2,3,4,5,6-pentafluorobenzoylbenzylidenetriphenylphosphorane, 13509-92-7; α-2,3,4,5,6-pentafluorobenzoyl-2,3,4,5,6-pentafluorobenzylidenetriphenylphosphorane, 13557-45-4; III, 13509-98-3; IV, 13509-99-4.

Acknowledgment.—The authors wish to express their gratitude to the National Institutes of Health for financial support of this research under Grant GM-12146.

Selective Demethylation of Deoxyanisoin. Mass Spectra of the Products

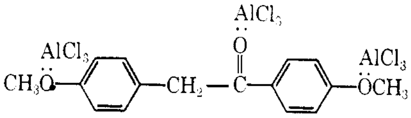
D. Lednicer and M. F. Grostic

Biochemical Research Division, The Upjohn Company, Kalamazoo, Michigan 49001

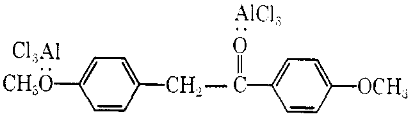
Received February 6, 1967

Recently, in connection with another problem, we had occasion to need sizable quantities of *p*-hydroxyphenyl *p*-methoxybenzyl ketone[1] (II). On the basis of previous work,[2] reaction of deoxyanisoin (I) with a limited amount of aluminum chloride would be expected to afford the desired phenol. We found, in fact, that, when deoxyanisoin was refluxed with 3 moles of aluminum chloride for 1.5 hr, the desired phenol was isolated in 30% yield accompanied by a major amount (25% by isolation) of the bisdemethylated product (III).[3] In an attempt to cut down the apparent overreaction, we cut the amount of aluminum chloride used back to 2 moles. The time required for the disappearance of starting material was in this case considerably longer (18 hr). To our surprise, the phenolic product of this reaction was not the known compound (II) but its hitherto unreported isomer (IV) (see section on mass spectra for structural proof and Scheme I).

These divergent reaction patterns can perhaps best be explained as a balance between thermodynamic and kinetic effects. Thus, the 3 moles of the Lewis acid probably complex with the three oxygens of the molecule (V). The electron-withdrawing carbonyl group *para* to the complexed ether group accelerates the rate of reaction of that group relative to the ether *para* to the methylene and leads to II. The use of an insufficient amount of aluminum chloride (2 moles) brings into play the relative basicities of the oxygens. The electron-releasing methylene group serves to render the ether *para* to that group more basic than that *para* to the carbonyl, resulting in a complex such as VI. The net effect is a reaction which, though much slower, leads to IV.



V



VI

Mass Spectra.—The isomers represented by II and IV involve a single interchange of two functional groups. Consequently, physical measurements such as the ultraviolet, infrared, or nmr spectra could not lead to unequivocal assignments of structures without some involved arguments. Mass spectrometry seemed uniquely appropriate for this structural assignment.

The partial mass spectra of compounds I–IV are shown in Table I. These data suggest fragmentation patterns for deoxyanisoin (I) and the bisdemethylated compound (III) such as those shown in Scheme II. The most intense peak in the spectrum of I (b, *m/e* 135) demonstrates the presence of a methoxyl *para* to the carbonyl group. It is of note that the analogous ion (b′) is the base peak of the spectrum of III and is observed 14 mass units lower at *m/e* 121 because the methyl group has been replaced by hydrogen.

A predominant peak at *m/e* 135 in the mass spectrum is thus diagnostic for the presence of ion b, and the presence of a methoxyl group *para* to the carbonyl

[1] W. Tadros, L. Ekladios, and A. B. Sakla, *J. Chem. Soc.*, 2351 (1954).

[2] T. R. Seshardri and G. B. Veukatasubramanian, *ibid.*, 1660 (1959).

[3] N. P. BuuHoi, M. Sy, and N. D. Xuong, *Bull. Chem. Soc. France*, 629 (1956).

SCHEME I

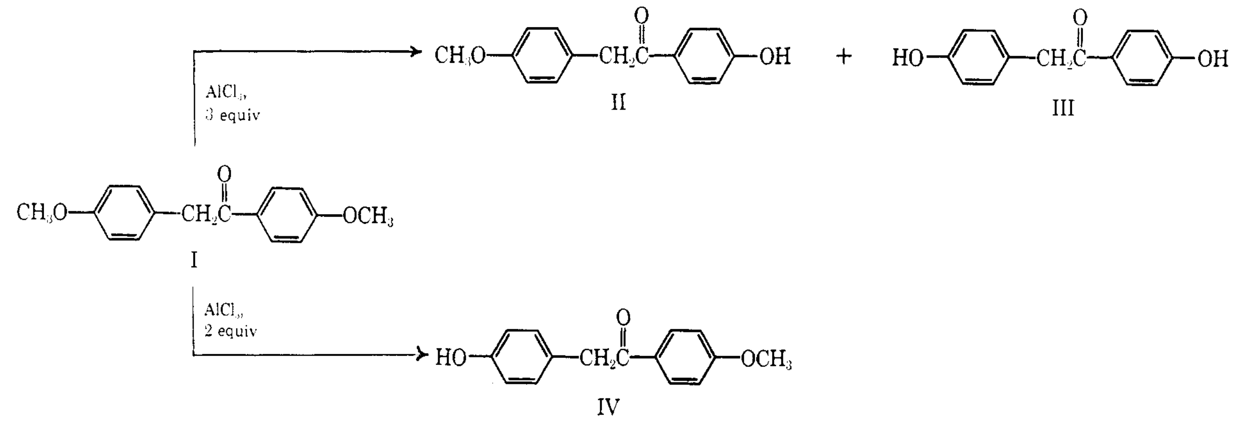


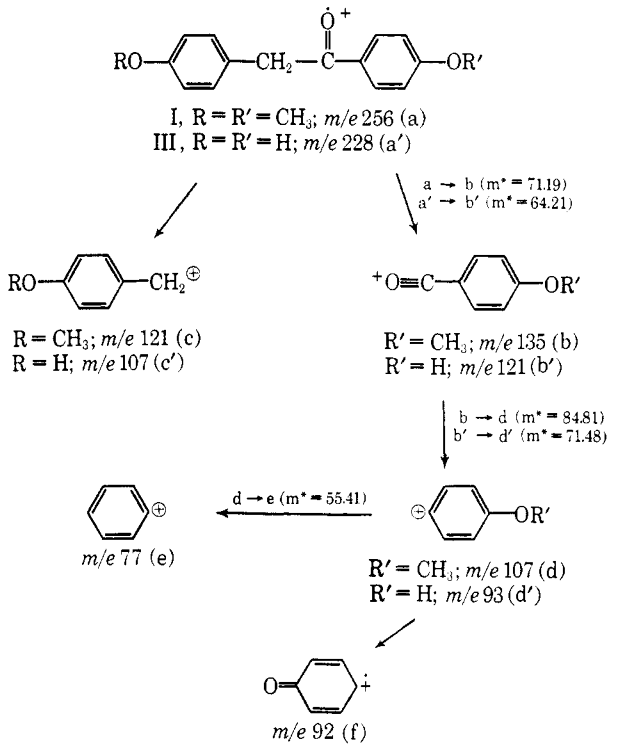
TABLE I

PARTIAL MASS SPECTRA—DEOXYANISOIN AND DERIVATIVES

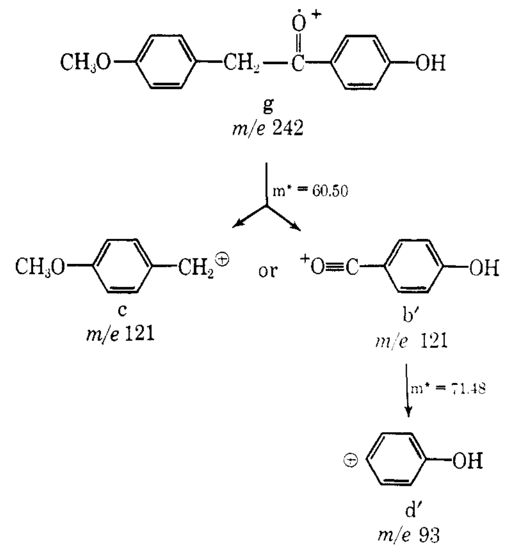
m/e	I (256)	II (242)	IV (242)	III (228)
	Compound (mol wt)			
39	0.5[a]	1.2	1.3	6.5
51	1.0	0.5	1.5	2.0
53	0.3	0.3	0.8	1.9
60	...	0.2	2.9	...
63	0.9	0.4	1.2	1.6
64	1.7	0.3	2.1	1.1
65	0.4	2.0	0.5	11.4
77	7.8	1.4	9.5	6.5
78	2.1	1.3	1.3	1.5
92	4.1	0.5	4.9	0.6
93	...	1.6	0.5	9.9
107	3.2	0.4	8.1	10.9
121	7.1	100	3.3[b]	100
122	0.5	6.1	0.2	6.2
135	100	2.9[c]	100	...
136	6.8	0.2	7.6	...
228	...	...	0.1	7.6
229	...	...	...	0.7
242	...	9.1	8.8	
243	...	1.4	1.4	
256	9.8			
257	1.6			

[a] Relative peak heights referred to base peak of spectrum as 100. [b] Suggests some compound II impurity. [c] Suggests some compound IV impurity.

SCHEME II



SCHEME III



group. By the same argument, the *m/e* 121 peak suggests a hydroxyl group in this *para* position and is further substantiated by the loss of 28 mass units (CO) accompanied by the corresponding metastable ion (*m/e* 71.48).[4,5]

The 242 molecular weight of the unexpected demethylation product shows that it was monodemethylated. On the basis of the predominant peak at *m/e* 135 we can unequivocally assign structure IV to this compound.

The base peak of the mass spectrum of compound II occurs at *m/e* 121 and can be represented in one of two ways (Scheme III).

The dominant pathway could not be ascertained on the basis of this spectrum alone. High-resolution mass spectrometry would supply this answer; however, on the basis of the spectra of the other three compounds studied, the most likely pathway would be g → b′ → d′. It is interesting to note that this one area of doubt has no effect upon the assignments of the structures.

---

(4) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, p 251.

(5) J. H. Beynon, R. A. Saunders, and A. E. Williams, "Table of *Meta*-Stable Transitions for Use in Mass Spectrometry," Elsevier Publishing Co., New York, N. Y., 1965.

Experimental Section[6]

Reaction of Deoxyanisoin with 3 Equiv of Aluminum Chloride.—A mixture of 12.8 g of deoxyanisoin and 20 g of aluminum chloride in 250 ml of benzene was heated under reflux for 1.5 hr. The mixture was then cooled in ice and treated with 200 ml of 2.5 *N* hydrochloric acid. The organic layer was diluted with ether and washed in turn with water and aqueous sodium bicarbonate. Thr organic solution was then extracted with 300 ml of 5% aqueous sodium hydroxide. The solid which was obtained when the extract was acidified was collected on a filter and dried. This was chromatographed on 1 l. of Florisil (elution with 15%, then 25% acetone in Skellysolve B[7]). There was obtained 4.25 g of the monophenol (mp 173-178°) followed by a mixture of mono- and bisphenols.

The former was recrystallized from aqueous methanol to give 4.02 g of *p*-hydroxyphenyl *p*-methoxybenzyl ketone (II), mp 175-178° (lit.[1] mp 175°).

The mixture was recrystallized from aqueous methanol to afford 2.80 g of the bisphenol (III), mp 215-219° (lit.[3] mp 215°).

Reaction of Deoxyanisoin wih 2 Equiv of Aluminum Chloride.—A mixture of 1.28 g of deoxyanisoin and 1.33 g of aluminum chloride in 20 ml of benzene was heated at reflux for 18 hr. The mixture was allowed to cool and treated with 15 ml of 2.5 *N* hydrochloric acid. Ether was added and the mixture shaken until the solid had all dissolved. The organic layer was separated and washed with water. This solution was extracted with 5% sodium hydroxide. Acidification of the extract afforded 0.85 g of the crude phenol. This was recrystallized twice from aqueous methanol to afford 0.60 g of *p*-hydroxybenzyl *p*-methoxyphenyl ketone (IV), mp 152-155°, ν_{max} 3400 and 1680 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.41; H, 6.06.

Registry No.—I, 120-44-5; II, 3669-46-3; III, 3669-47-4; IV, 13619-63-1.

---

[6] Melting points are uncorrected and recorded as obtained on a Thomas-Hoover melting point apparatus. The mass spectra were recorded using an Atlas CH4 instrument equipped with a T04 source; ionizing potential was 70 ev.

[7] A petroleum fraction, by 61-70°, marketed by the Skelly Oil Co.

The Identification of Dehydrocorydalmine and a New Protoberberine Alkaloid, Stepharanine, in *Stephania glabra* Tubers[1]

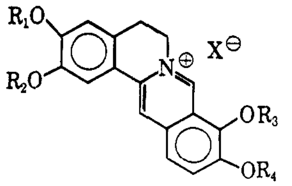
Raymond W. Doskotch, M. Younas Malik, and Jack L. Beal

College of Pharmacy, The Ohio State University,
Columbus, Ohio 43210

Received April 21, 1967

Examination of the quaternary alkaloid fraction from the tubers of *Stephania glabra* (Menispermaceae) resulted in the isolation of six crystalline alkaloids.[2] Four of these have been identified as the ubiquitous aporphine magnoflorine and the three protoberberines palmatine (I), jatrorrhizine (II), and columbamine (III). This report is on the characterization of the remaining two optically inactive alkaloids whose isolation and some general properties have been reported. They were previously designated as alkaloids A and B. Alkaloid A has been found to be dehydrocorydalmine (IV) and alkaloid B, a new alkaloid, has been named stepharanine (V).

Alkaloid A as the chloride salt, mp 220-221° dec, analyzed for $C_{20}H_{20}NO_4Cl \cdot H_2O$ and for the presence of three methoxy groups. The ultraviolet spectrum was characteristic of the protoberberine alkaloids[3] and the phenolic nature was evidenced by bathochromic shifts in the presence of dilute base. The infrared absorption spectra taken in a KBr pellet supported the presence of a hydroxyl group by the broad absorption bands at 3440 and 3500 cm^{-1}.



I, $R_1, R_2, R_3, R_4 = CH_3$
II, $R_1 = H; R_2, R_3, R_4 = CH_3$
III, $R_2 = H; R_1, R_3, R_4 = CH_3$
IV, $R_4 = H; R_1, R_2, R_3 = CH_3$
V, $R_2, R_4 = H; R_1, R_3 = CH_3$
VI, $R_3 = H; R_1, R_2, R_4 = CH_3$

The nmr spectrum was most informative showing six aromatic protons at δ 7.10 (1 H, singlet), 7.68 (1 H, s), 7.96 (2 H, s), 8.59 (1 H, s), and 9.58 ppm (1 H, s), three methoxy groups centered at 4.09, 4.15, and 4.28 ppm, and two triplets at 3.42 and 5.02 with $J = 6$ cps. The nmr spectrum of palmatine (I) determined under the same conditions showed six aromatic protons at 7.09 (1 H, s), 7.69 (1 H, s), 8.07 (2 H, s), 8.60 (1 H, s), and 9.68 (1 H, s), four methoxy peaks at 4.07, 4.13, 4.19, and 4.34, and two triplets at 3.40 and 5.01 ($J = 6$ cps). These results are consistent with alkaloid A having the same oxygenation pattern as palmatine and possessing three methoxy groups and one phenolic group. Methylation of alkaloid A chloride by dimethyl sulfate in aqueous sodium bicarbonate solution yielded palmatine chloride identical in all respects (infrared, ultraviolet, tlc, and mixture melting point) with an authentic sample and confirming the substitution positions.

The position of the phenolic group remained to be settled. Since jatrorrhizine (II) and columbamine (III), two other monophenolic protoberberines were already known from this source, alkaloid A must be either palmatrubine (VI)[4] or dehydrocorydalmine (IV).[5] Palmatrubine iodide was prepared[6] from palmatine iodide by fusion with urea and found to be different from alkaloid A iodide. Consequently alkaloid A must be dehydrocorydalmine. The iodide salt of our compound melts with decomposition at 195° while Imaseki and Taguchi reported 228-230° dec. We were unable to prepare any other common derivative owing to insufficient material nor were we able to obtain a sample of dehydrocorydalmine for a direct comparison.

Alkaloid B as the chloride salt, mp 274-275° dec, analyzed for $C_{19}H_{18}NO_4Cl \cdot H_2O$ and appeared to be another phenolic protoberberine alkaloid from examination of the ultraviolet and infrared absorption spectra. Again, the nmr spectrum was most informative, showing six aromatic protons at δ 7.03 (1 H, singlet), 7.71 (1 H, s), 7.94 (2 H, s), 8.52 (1 H, s), and 9.55 ppm (1 H,

---

[1] Supported by Grant GM-05640 from the National Institutes of Health, U. S. Public Health Service.

[2] M. T. Wa, J. L. Beal, and R. W. Doskotch, *Lloydia*, in press.

[3] A. W. Sangster and K. L. Stuart, *Chem. Rev.*, **65**, 69 (1965).

[4] E. Spath and G. Burger, *Ber.*, **59**, 1486 (1926).

[5] I. Imaseki and H. Taguchi, *J. Pharm. Soc. Japan*, **82**, 1214 (1962).

[6] Palmatrubine iodide, mp 234-236° dec, was prepared from palmatine iodide by fusion with urea according to Spath and Burger,[4] but the temperature was maintained between 170 and 180°. Methylation of the product with dimethyl sulfate gave palmatine iodide and reduction with sodium borohydride gave tetrahydropalmatrubine, mp 146-148° (lit.[4] mp 148-149°).