Summary

1. The relation between the structure of certain polyhydric phenols and their reactivity with respect to sodium antimonyl tartrate has been studied.

2. The introduction of substituted and unsubstituted alkyl groups into the carboxyl group of gallic acid has little influence on this reaction.

3. The replacement of one of the hydroxyl hydrogen atoms of pyrogallol or gallic acid by an organic group prevents the reaction from taking place.

4. Certain benzylidene derivatives of 2,3,4-trihydroxybenzaldehyde do not react with sodium antimonyl tartrate.

5. The composition of the products depends upon the experimental conditions which are used.

6. Arsphenamine condenses readily with the antimonyl derivative of 2,3,4-trihydroxybenzaldehyde.

7. These antimonials are trypanocidally active.

BOSTON 17, MASSACHUSETTS

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

THE SEED AND OIL OF JOHANNESIA PRINCEPS

BY GASTAO ETZEL[1] AND C. G. KING

RECEIVED JANUARY 18, 1926 PUBLISHED MAY 5, 1926

Johannesia Princeps is a Brazilian tree belonging to the family Euphorbiaceae. It grows rapidly and equally well in a great variety of soils and produces an abundance of nuts which are used in Brazil for medicinal purposes. The kernels are almond-like in consistency, 10 to 20 g. each in weight, and have an agreeable flavor. By cold pressing, or extracting them with ether, a clear, slightly yellowish-green oil is obtained. The nuts and oil have been widely used for their laxative effect, and the latter has been used as a drying oil. Highly satisfactory results have been reported upon the use of the oil as a cathartic, by several authors,[2] who state that its particular advantages are agreeable flavor and odor, low viscosity, no intestinal irritation, no nausea and a potency about four times that of castor oil.

B. Niederstadt and Th. Peckol[3] made partial analyses of the oil, and M. Oliveira[2] reported the presence of an active principle (johannisin), analogous to ricinin, in the embryo of the seed.

[1] This paper is based upon a thesis submitted to the Graduate School of the University of Pittsburgh by Gastao Etzel in partial fulfilment of the requirements for the degree of Master of Science.

[2] Anon., *New Remedies*, **10**, 260–1 (1881); *Pharm. J. Trans.*, **41**, 380 (1881–1882); *Monit. Pharm.*, **1881**, 156.

[3] Niederstadt and Peckol, *Ber. Pharm. Ges.*, **15**, 225 (1905).

The present investigation was undertaken to determine (a) the percentage of oil in the seed, (b) the physical properties of the oil, (c) the chemical properties of the oil and its composition, and (d) the composition of the press cake.

Preparation of the Oil

The seeds used in this investigation were supplied from S. Paulo, Brazil, and were air-dried. The first step in the process was the removal of shells from the seeds; the latter were then passed through a nut grinder, weighed and subjected to a pressure of 200 atmospheres. The oil thus obtained was filtered, weighed and kept in glass-stoppered bottles; average yield, 26.6%. The oil from a small portion of the cake was extracted with ether in Soxhlet extractors; average yield, 30.4%. Extraction was also applied to small portions of the ground nuts which were not subjected to cold pressing; yield, 55.7%.

Physical Properties

The oil was clear and has a light yellowish-green color, characteristic of vegetable oils. It was not disagreeable to the taste.

The specific gravity, determined by the Westphal balance and pycnometer, was found to be 0.9257 at 15.5° and 0.9229 at 20°. The index of refraction determined by means of an Abbé refractometer was 1.4770 at 15° and 1.4750 at 20°.

Chemical Properties

1. **Chemical Characteristics.**—The chemical characteristics given in Table I were determined for the purpose of ascertaining the general composition of the oil, as well as to furnish a basis for comparison with other oils. The values given in this and in the following tables are the averages of two determinations which checked closely.

TABLE I

CHEMICAL CHARACTERISTICS

Iodine No. (Hanus)	115.67	Acetyl value	8.75
Saponification No.	192.15	Reichert-Meissl No.	1.2
Ester No.	186.71	Polenske No.	0.345
Acid value	5.44	Unsaponifiable matter	1.17

It is evident from the data that the oil of *Johannesia Princeps* is not of the same type as castor oil or croton oil. A phytosterol was separated from the unsaponifiable matter having a melting point of 131° after recrystallizing four times from alcohol. The qualitative tests of Halphen, Baudouin and Settimi were negative.

2. **Separation of Fatty Acids.**—The Gusseroff and Varrentrapp method[4] was used for the separation of solid, saturated fatty acids from the

[4] Leathes and Raper, "The Fats," Longmans, Green and Co., 1925, p. 82.

liquid unsaturated acids. The method involves the conversion of acids into their lead salts which, in the case of saturated acids, are insoluble in ethyl ether, while those of the unsaturated acids are soluble. The separation of the different unsaturated acids was based upon bromination[5] which produced a difference in the solubility of the bromides in ethyl and petroleum ethers.

TABLE II

SEPARATION OF THE FATTY ACIDS

	Wt., g.		Indicated value, %	Corrected value, %
Sample of oil	4.2032		...	...
Unsaturated acids	3.3341		79.30	80.45
Saturated acids	0.3756		8.93	7.79
Bromides insoluble in ethyl ether	.0595		...	...
Bromides insoluble in petroleum ether	2.4110		...	...
Calculated as linolic acid	1.1200		26.60	27.90
Bromides soluble in petroleum ether	3.3695		...	...
Calculated as oleic acid	2.1500		51.10	52.24
Iodine No. (Hanus) of unsaturated acids		147.70		
Saponification No. of unsaturated acids		196.10		
Iodine No. of saturated acids		11.43		
Saponification No. of saturated acids		222.80		

Since the separation of the bromides is not sharp and varies considerably with different oils, it is necessary to determine the bromine content of each fraction. The percentage of each type of bromide can then be calculated for each precipitate. The Carius method of analysis was followed in this work.

TABLE III

ANALYSES OF BROMIDES

	Bromides, g.	AgBr, g.	Bromine, %
Precipitate from ethyl ether	0.3447	0.1886	52.71
Precipitate from petroleum ether	.1505	.1865	52.70
Soluble in petroleum ether	.1917	.1930	42.08

The calculated values for the pure bromides are as follows: dibromostearic acid, 36.18; tetrabromostearic acid, 53.33. From these data it is evident that the precipitate from ethyl ether was a tetrabromide, and that some tetrabromide separated with the dibromide. An indefinite amount of unsaturated fatty acid always goes into the saturated fraction. The amount present can be estimated from the iodine number, and adds another small correction to the oleic fraction. From the values given, this correction is 0.0481 (1.15%), which was subtracted from the total saturated acids. The "corrected values" in Table II are based upon the above data.

3. Composition of the Seed and Fat-free Cake.—From the analyses given in Table IV it is evident that the press-cake has a high nitrogen and

[5] Ref. 4, p. 86.

phosphorus value as a fertilizer and, providing the toxic principle could be removed, might be a valuable feed.

TABLE IV

COMPOSITION OF SEED AND FAT-FREE CAKE

	Fat-free cake, %	Original seed, %
Oil	...	56.89
Moisture	5.27	2.21
Ash	11.7	5.20
Crude fiber	4.84	2.09
Nitrogen	10.05	4.33
Protein (N × 6.25)	62.84	27.08
Carbohydrates (by difference)	15.44	6.56
Phytin $C_6H_6O_6(PO(OH)_2)_6$ (Heubner-Stadler) (Included in ash and carbohydrate)	13.29	5.70

Summary

1. The amount of oil in the seeds of *Johannesia Princeps* was determined by cold pressing and by extraction with ether.

2. The physical and chemical properties of the oil were determined, and the fatty acids separated. It was found to be in the class of "semi-drying" oils, and of a different type than the common cathartic oils.

3. Analysis of the press cake showed that it has possibilities for use as a fertilizer material.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

METHYLBIPHENYLS

BY M. GOMBERG AND J. C. PERNERT[1]

RECEIVED JANUARY 27, 1926 PUBLISHED MAY 5, 1926

Recently Gomberg and Bachmann[2] have described a procedure whereby a number of unsymmetrical biaryls, hitherto difficult or impossible of preparation, have been obtained in satisfactory yields.

The literature on methylbiphenyls is not extensive, and the preparation and purification of these hydrocarbons has been very difficult. In some cases the constitutions of the derivatives remain wholly unknown, in others they are not conclusively proved and are open to question. The main purpose of this investigation has been to work out suitable syntheses for a few of these hydrocarbons and to prepare some of the derivatives and obtain convincing proof of their constitutions. In connection with this, we have accumulated a number of facts which permit a further insight into the

[1] The material here presented is from a dissertation submitted by J. C. Pernert to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1925.

[2] Gomberg and Bachmann, THIS JOURNAL, **46**, 2339 (1924).