amounted to 100 ml., and the water layer (which could be redistilled), to 110 ml. Proper design of the distilling head permits the direct return of the water layer to the column so that water-saturated butanol alone is the offtake. If anhydrous butanol is desired, the butanol layer may be distilled, and since the composition is in the Y to 100 region of Figure 2, the azeotrope is collected in the distillate and anhydrous butanol is left behind.

Discussion

The method of recovery selected for industrial use would undoubtedly be determined by the cost of equipment, the cost of heat, and rapidity. Each of the processes described has advantages peculiar to itself. Both methods permit quantitative recovery of butanol with no interference from lignin or alkali. Neither method eliminates consideration of other methods, such as changing the temperature of the water layer to decrease solubility or salting out. The chief significance of the data reported here is that the lignin and alkali occurring in butanol pulping liquors do not interfere with the separation, and that with proper equipment industrial operation can expect quantitative recovery of butanol.

Literature Cited

(1) Bailey, A. J., Ind. Eng. Chem., Anal. Ed., 13, 487-91 (1941).
(2) Bailey, A. J., *Pacific Pulp & Paper Ind.*, 14, 24-7 (March, 1940).
(3) Bailey, A. J., *Paper Trade J.*, 110, TS 15-18 (Jan. 11, 1940).
(4) Bailey, A. J., U. S. Patent 2,166,540 (July 18, 1939).
(5) Stockhardt, J. S., and Hull, C. M., Ind. Eng. Chem., 23, 1438 (1931).

Contribution from the Department of Chemistry and Chemical Engineering and the Lignin & Cellulose Research Laboratories, University of Washington.

Pyrogallol Derivatives as Gasoline Antioxidants

W. W. SCHEUMANN AND JOHN H. HASLAM
Cities Service Oil Company, Bartlesville, Okla.

Pyrogallol and its alkyl derivatives have found only a limited use as gasoline antioxidants because of the ease with which they are extracted from gasoline by water. 5-Alkylpyrogallol-1,3-dimethyl ethers in which the alkyl group contains 5 or more carbon atoms are more powerful antioxidants than the corresponding 5-alkylpyrogallols and also have more advantageous solubilities.

The introduction of a second alkyl group to the ring of 5-methylpyrogallol-1,3-dimethyl ether resulted in a small improvement in antioxidant effectiveness, but the introduction of the third alkyl group gave a product with only slight antioxidant properties.

The isolation of 5-methylpyrogallol-1,3-dimethyl ether and 5-propylpyrogallol-1,3-dimethyl ether in pure form from hardwood distillate is described. These two compounds were responsible for a substantial part of the antioxidant properties of a hardwood distillate boiling at 217-310 C.

CRACKED gasoline deteriorates in storage, and a resinous gum forms in appreciable quantities. This gum will cause serious difficulties in internal combustion motors, and it is therefore common practice to add small quantities of antioxidants or gum inhibitors to such gasolines during refining.

The antioxidant properties of various phenolic compounds have been extensively investigated in recent years, and many are being successfully used. In most operations the antioxidant is added to the gasoline immediately after it has been treated, at which time the gasoline often has suspended in it small particles of water in the form of a haze. This water settles out in the storage tanks, and if the antioxidant used is water soluble, a considerable portion is extracted from the gasoline. The relative solubilities of antioxidants in water and gasoline are of great importance, therefore, and must be considered along with their inhibiting effectiveness.

Unfortunately many phenols which are powerful antioxidants are unsatisfactory from the solubility standpoint. In general, a comparatively large hydrocarbon group on the phenolic molecule is advantageous, for it increases the solubility in gasoline and decreases the solubility in water. The presence of hydroxyl or some other polar group in the molecule has the opposite effect and is unsatisfactory from the solubility standpoint. The polyhydroxy benzenes, in general, are more powerful antioxidants than the monohydroxy compounds; thus the gum-inhibiting effectiveness increases from phenol to catechol to pyrogallol, but at the same time the solubility becomes less favorable. Pyrogallol is a powerful inhibitor, but its three hydroxyl groups cause it to be easily extracted from gasoline by water; consequently it has not been extensively used commercially. These unfortunate solubility characteristics can be remedied to some extent by the addition of alkyl groups to the molecule; and this investigation is concerned with these alkylpyrogallol derivatives.

Effect of Size of Alkyl Group

Conversion of one or more of the hydroxyl groups of pyrogallol to methyl ethers is advantageous from the standpoint of solubility, for this not only adds alkyl groups to the molecule but also converts polar to nonpolar groups. Unfortunately the inhibiting effectiveness of pyrogallol is greatly lowered by such a conversion of one or two hydroxyl groups, and the conversion of all three produces pyrogallol trimethyl ether which is not a phenol and has no inhibiting power.

In this investigation the effect of the addition of alkyl groups to the inhibiting effectiveness of pyrogallol and its 1,3-dimethyl ether was determined. The size of the alkyl group attached was found to influence greatly both compounds but in opposite directions. As the alkyl group became larger, its effect on pyrogallol was to decrease the inhibiting power, but on pyrogallol-1,3-dimethyl ether an increase in size of the alkyl group caused an increase in the inhibiting effectiveness. The alkyl group in each case was in the 5 position.

The effect of the size of the alkyl group attached to the 5 position of pyrogallol and pyrogallol-1,3-dimethyl ether is shown in Table I. When these results are graphed (Figure 1), it may be seen that the inhibiting quality of pyrogallol-1,3-dimethyl ethers containing an alkyl group smaller than amyl could be made more effective by splitting the ethers to the corresponding pyrogallols. This has been done (*7*, *8*) with hardwood distillates, the inhibiting power of which is due, in substantial part, to 5-methyl- and 5-propylpyrogallol-1,3-dimethyl ethers. Such conversion, however, produces a more water-soluble product and thus is unsatisfactory from this standpoint.

Table I. Effect of Size of Alkyl Group Attached to 5 Position

Antioxidant (20 Mg./100 Cc.)	Induction Period Increase over Gasoline Blank, Min.
Pyrogallol	890
Pyrogallol-1,3-dimethyl ether	170
5-Methylpyrogallol	575
5-Methylpyrogallol-1,3-dimethyl ether	260
5-Propylpyrogallol	435
5-Propylpyrogallol-1,3-dimethyl ether	330
5-Caprylpyrogallol	295
5-Caprylpyrogallol-1,3-dimethyl ether	475

Synthetic alkyl pyrogallol inhibitors in which the alkyl group is amyl or larger can be best used as the 1,3-dimethyl ethers, for these are not only more powerful inhibitors but they are also much less soluble in water and more soluble in gasoline than the corresponding pyrogallols. Several patents (*2*, *5*, *13*) have been issued on alkyl pyrogallols as gum inhibitors, but apparently none has taken advantage of the increased inhibiting effectiveness and more advantageous solubility of the dimethyl ethers.

Effect of Second and Third Alkyl Groups

The effect of a second and third alkyl group on the ring of 5-alkylpyrogallol-1,3-dimethyl ethers was determined; Table II shows the results of adding one and two amyl groups.

Table II. Effect of Adding One and Two Amyl Groups

Antioxidant (40 Mg./100 Cc.)	Induction Period Increase over Gasoline Blank, Min.
5-Methylpyrogallol-1,3-dimethyl ether	430
5-Methyl-6-amylpyrogallol-1,3-dimethyl ether	485
5-Methyl-4,6-diamylpyrogallol-1,3-dimethyl ether	40

The addition of one alkyl group to this compound, apparently producing 5-methyl-6-amylpyrogallol-1,3-dimethyl ether, improved the inhibiting effectiveness only slightly; and the addition of the second amyl group, producing 5-methyl-4,6-diamylpyrogallol-1,3-dimethyl ether, caused the material to lose practically all of its antioxidant properties. All six positions of the ring are substituted in the latter compound. These compounds are not described in the literature, and consequently their structure could not readily be proved. They were produced by a reaction between 5-methylpyrogallol-1,3-dimethyl ether and *tert*-amyl chloride in the presence of zinc chloride.

The boiling points of the products were higher than those of the original material, and the molecular weight agreed with the theoretical. That the one hydroxyl group remained unreacted was shown by the formation of a sodium salt. It seems fairly certain that the structure was as represented.

The introduction of the second and third alkyl groups to the ring would result in a compound of still more favorable solubility, but the improvement would probably be less than that obtained from the first group. A patent (*4*) was issued on the improvement in inhibiting effectiveness of hardwood distillates by alkylation; but this may have been due to the alkylation of phenols other than the pyrogallol ethers, for apparently only a slight improvement at best could be obtained by alkylation of 5-methyl- and 5-propylpyrogallol-1,3-dimethyl ethers.

Isolation of Ethers from Hardwood Distillates

A new procedure was used to recover 5-methyl- and 5-propylpyrogallol-1,3-dimethyl ethers in pure form from hardwood distillate. A close fraction of distillate was extracted with hot 10 per cent sodium hydroxide solution and allowed to settle, and the hot extract was drawn off. On cooling, the sodium salt of the 5-alkylpyrogallol-1,3-dimethyl ethers precipitated. Many investigators (*1*, *6*, *9–12*) have reported the presence of 1,3-dimethyl ethers of 5-methyl- and 5-propylpyrogallol in hardwood distillates since Hofmann (*3*) first described their isolation; and although the comparative insolubility of the sodium salt has been mentioned several times, this property apparently has not been generally utilized in their purification. Extraction with caustic solutions separates phenols from neutral hydrocarbons present in hardwood distillates, but crystallization of the sodium salts of these pyrogallols also gives a separation from small quantities of other phenols and acidic materials present. This comparative insolubility of the sodium salts of pyrogallol-1,3-dimethyl ethers was found to be general for all those used in this investigation and was very helpful in their purification. Since the procedure was adequate, no attempt was made to increase the efficiency of the process, and it is possible that a larger yield of both 5-methyl- and 5-propylpyrogallol-1,3-dimethyl ethers can be obtained under slightly different conditions, such as the use of a more concentrated sodium hydroxide solution in their extraction. Increased purity probably can be obtained by recrystallization of the sodium salt.

Figure 2 shows that the antioxidant property of hardwood distillate (boiling at 217–310° C.) is largely due to 5-methyl- and 5-propylpyrogallol-1,3-dimethyl ethers. The sharp curve upward in inhibiting effectiveness at the seventh fraction coincides with the appearance of 5-methylpyrogallol-1,3-dimethyl ether in the distillate. Recovery of 5-methyl- and 5-propylpyrogallol-1,3-dimethyl ethers showed that they comprise 86 per cent of the material in fractions 8 to 13, inclusive. The remaining 14 per cent was made up chiefly of neutral hydrocarbons.

Experimental Procedure

5-Methylpyrogallol-1,3-dimethyl Ether. A sample of commercial hardwood distillate boiling at 217–310° C. was fractionated at 10 mm. pressure, and 10° fractions were taken. The fraction boiling at 130–140° C. at 10 mm. was placed in a large separatory funnel and extracted with hot 10 per cent sodium hydroxide solution. Steam was used to agitate the mixture and maintain the temperature at 95–100° C. The caustic extract was drawn off while still hot, and on cooling to room temperature, a considerable quantity of the sodium salt of 5-methylpyrogallol-1,3-dimethyl ether crystallized and was filtered off. On chilling in an ice bath, a second crop of crystals separated and were combined with the first. Exposure of this caustic solution to the air was avoided as much as possible, for the dissolved phenols oxidized rapidly and the solution darkened visibly. The separatory funnel was kept closed during the extraction, and the extract was drawn into a closed flask for cooling. The dry sodium salts of these phenols appeared to be fairly stable, however, and did not darken noticeably after exposure to air for two or three days.

The combined crystals were shaken with dilute sulfuric acid, and the freed 5-methylpyrogallol-1,3-dimethyl ether was separated as an oil. This oil was drawn off, dried, and distilled at 10 mm. pressure. That portion boiling from 134–138° C. was kept. It was identified by the following tests:

	Product	5-Methylpyrogallol-1,3-dimethyl Ether
Boiling point, ° C.	262–265	265
Melting point, ° C.	28–30	29–30
Carbon, %	64.7	64.3
Hydrogen, %	7.3	7.1
Methoxyl, %	37.2	36.9
Mol. weight	164	168

5-PROPYLPYROGALLOL-1,3-DIMETHYL ETHER. This ether was isolated from hardwood distillate in a manner identical to that described for the isolation of 5-methylpyrogallol-1,3-dimethyl ether except that a fraction boiling from 150–160° C. at 10 mm. pressure was the starting material. The final product boiled at 154–158° C. at 10 mm. Its identity was established by the following tests:

	Product	5-Propylpyrogallol-1,3-dimethyl Ether
Boiling point, ° C.	284–287	283–289
Carbon, %	67.1	67.3
Hydrogen, %	8.2	8.2
Methoxyl, %	31.1	31.6
Mol. weight	194	196

5-METHYLPYROGALLOL. 5-Methylpyrogallol-1,3-dimethyl ether was refluxed with 40 per cent hydrobromic acid for 3 hours; the resulting oil layer separated, dried, and distilled. That portion boiling at 170–175° C. at 10 mm. pressure was used:

	Product	5-Methylpyrogallol
Boiling point, ° C.	302–308	...
Melting point, ° C.	112	119; 129
Methoxyl, %	0	0
Silver nitrate soln. (cold)	Reduced	Reduced

5-PROPYLPYROGALLOL. 5-Propylpyrogallol-1,3-dimethyl ether was refluxed for 3 hours with 40 per cent hydrobromic acid, and the resulting oil layer was separated, dried, and distilled. That portion boiling at 170–175° C. at 10 mm. pressure was used:

	Product	5-Propylpyrogallol
Boiling point, ° C.	307–313	...
Melting point, ° C.	75	79–80
Methoxyl, %	0	0
Silver nitrate soln. (cold)	Reduced	Reduced

PYROGALLOL-1,3-DIMETHYL ETHER. To a cold solution of 80 grams of sodium hydroxide in 500 cc. of water were added 50 grams of pyrogallol. The mixture was agitated until the pyrogallol dissolved, and the whole was poured into a 1000-cc. separatory funnel. Ninety-four grams (70 cc.) of methyl sulfate were then added in five portions with shaking and standing after each addition. A precipitate of sodium-1,3-dimethylpyrogallate separated and was filtered. The filtrate was refluxed for 2 hours and cooled, and a second crop of crystals separated. The combined crystals were then shaken with dilute sulfuric acid, and the oil which separated was drawn off, dried, and distilled. That portion boiling at 260–265° C. was used. This boiling range showed that the product was the 1,3-dimethyl ether for the boiling point of this compound is 263° C., while the 2,3-dimethyl ether boils at 233° C.:

	Product	Pyrogallol-1,3-dimethyl Ether
Boiling point, ° C.	260–265	263
Methoxyl, %	39.5	40.3
Silver nitrate soln. (cold)	No reaction	No reaction

5-CAPRYLPYROGALLOL-1,3-DIMETHYL ETHER. A procedure similar to that for pyrogallol-1,3-dimethyl ether was followed for 5-caprylpyrogallol-1,3-dimethyl ether. 5-Caprylpyrogallol, from the National Aniline and Chemical Company, was the starting material. That portion of the reaction product boiling at 190–195° C. at 3 mm. pressure was saved. The original material boiled at 208–216° C. at 3 mm. The positions of the methoxyl groups in the product were not definitely established since 5-caprylpyrogallol dimethyl ethers are not described in the literature. However, since this procedure produced the 1,3-dimethyl ether of pyrogallol, it seems reasonable to assume that the 1,3 positions were methylated here also. The methoxyl content of the product was found to be 23.2 per cent; the methoxyl content of 5-caprylpyrogallol-1,3-dimethyl ether is 23.3 per cent.

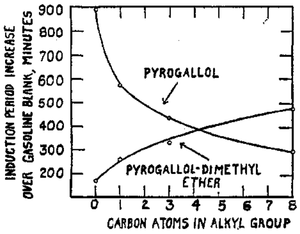

FIGURE 1. EFFECT OF SIZE OF ALKYL GROUP ON ANTIOXIDANTS

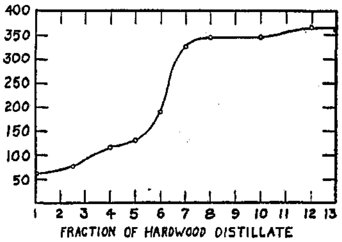

FIGURE 2. ANTIOXIDANT PROPERTIES OF HARDWOOD DISTILLATE

MONO- AND DIAMYL-5-METHYLPYROGALLOL-1,3-DIMETHYL ETHERS. Three moles of *tert*-amyl chloride, one mole of 5-methylpyrogallol-1,3-dimethyl ether, and 200 cc. of a paraffinic naphtha (specially treated with aluminum chloride to make it unreactive) were placed in a three-neck flask equipped with mercury-sealed stirrer, condenser, and hydrochloric acid gas trap. One-half mole of anhydrous, powdered zinc chloride, was added, and the whole gently refluxed with agitation for about 3 hours.

The contents of the flask were brought to room temperature, poured into an equal volume of water, and agitated vigorously until hydrolysis was complete. The aqueous layer was discarded, and the naphtha layer extracted with 10 per cent hot sodium hydroxide solution. On cooling, a small quantity of crystals separated and was filtered off. On acidification, these gave an oil boiling at 156–160° C. at 3 mm. pressure. Its molecular weight was 301. The boiling point of 5-methyl-4,6-diamylpyrogallol-1,3-dimethyl ether is not reported in the literature, but its molecular weight is 308. The methoxyl content was found to be 13.3 per cent, the theoretical for 5-methyl-4,6-diamylpyrogallol-1,3-dimethyl ether being 13.8 per cent.

The caustic filtrate was acidified, and the oil separating was distilled under reduced pressure. That portion boiling at 125–130° C. at 3 mm. was saved. Its molecular weight was 230. The molecular weight of 5-methyl-6-amylpyrogallol-1,3-dimethyl ether is 238. The methoxyl content of the product was found to be 19.8 per cent, the theoretical for 5-methyl-6-amylpyrogallol-1,3-dimethyl ether being 20.1 per cent.

TESTS OF ANTIOXIDANT EFFECTIVENESS. From 30 to 80 mg. of the antioxidant to be tested were accurately weighed in a 250-cc. glass-stoppered Erlenmeyer flask and dissolved in 5 cc. of C. P. acetone. The amount of gasoline required to make the desired antioxidant concentration was then poured in; the flask was tightly stoppered and agitated thoroughly.

Induction periods were determined by a slight modification of A. S. T. M. method D525-39T (bomb designed to hold conventional 4-ounce sample bottle) which has been found in numerous checks to duplicate results of the A. S. T. M. method.

The gasoline used in determining induction periods given in Tables I and II and Figure 1 was a doctor-sweetened 100 per cent cracked stock with a blank induction period of 160 minutes. The gasoline used in determining induction periods given in Figure 2 was a doctor-sweetened, 100 per cent cracked stock with a blank induction period of 170 minutes.

Summary

The gasoline antioxidant properties of 5-alkylpyrogallols and their 1,3-dimethyl ethers were investigated. The size of the alkyl group was found to affect greatly the inhibiting power of both the pyrogallol and its di-ether but in opposite directions. As the alkyl group on the di-ether became larger, the inhibiting effectiveness increased, but an increase in size of the alkyl group on pyrogallol decreased its effectiveness. When the alkyl group contained 4 carbon atoms or less, the pyrogallol was the more effective inhibitor, but when the alkyl group contained over 4 carbon atoms, the 1,3-dimethyl ether was the more effective. The 1,3-dimethyl ethers have much more advantageous solubility characteristics than the corresponding pyrogallols.

The antioxidant properties of a hardwood distillate, boiling at 217–310° C., were found to be substantially due to 5-methyl- and 5-propylpyrogallol-1,3-dimethyl ethers.

5,6-Dialkylpyrogallol-1,3-dimethyl ethers were only slightly more effective inhibitors than the corresponding 5-alkylpyrogallol-1,3-dimethyl ether; and the 4,5,6-trialkylpyrogallol-1,3-dimethyl ethers tested had practically no inhibiting power.

A method is described for isolating 5-methyl- and 5-propylpyrogallol-1,3-dimethyl ethers in a pure form from hardwood distillates.

Literature Cited

(1) "Allen's Commercial Organic Analysis", 4th ed., Vol. III, pp. 346–62, Philadelphia, P. Blakiston's Son & Co., 1917.
(2) Berger, H. G., and Mygaard, E. M., U. S. Patent 2,114,437 (April 19, 1938).
(3) Hofmann, A. W., *Ber.*, **11**, 333 (1878).
(4) Ipatieff, V. N., U. S. Patent 2,058,881 (Oct. 27, 1936).
(5) *Ibid.*, 2,099,738 (Nov. 23, 1937).
(6) Leger, F., and Hibbert, H., *Can. J. Research*, **16B**, 151 (1938).
(7) Lowry, C. D., and Dryer, C. G., U. S. Patent 2,083,197 (June 8, 1937).
(8) Morrell, J. C., *Ibid.*, 2,123,541–2 (July 12, 1938).
(9) Schultes, H., *Ber.*, 69, 1870–3 (1936).
(10) Sumarakov, V. P., and Stepanova, M. I., *J. Applied Chem.* (U. S. S. R.), **10**, 1248–59 (1937).
(11) Sumarakov, V. P., and Ugryumov, V. D., *Lesokhim Prom.*, 4, No. 1, 5–8, No. 2, 3–6 (1935).
(12) Ugryumov, V. D., *Ibid.*, 2, No. 3, 19–21 (1933).
(13) Wilson, C. P., U. S. Patent 2,084,754 (June 22, 1937).

Preparation of Pure Geraniol

HOWARD A. JONES AND JOHN W. WOOD
Bureau of Entomology and Plant Quarantine, U. S. Department of Agriculture, Beltsville, Md.

GERANIOL has been separated and purified by means of its calcium chloride addition compound for many years. The method as described by Gildemeister and Hoffman (*1*) and by Parry (*3*) involves direct mixing of calcium chloride with the oil or a suitable fraction, followed by separation of the uncombined material by a water-immiscible solvent. This method is laborious and the yields are poor.

It has been found that treatment of a hexane solution of the geraniol-containing oil with calcium chloride, together with certain other changes in technique, effects a marked improvement, especially as to ease of handling. Pentane was tried, but hexane was more satisfactory. Practically complete conversion to the addition compound was obtained after 2-hour stirring. The modified method gave a product of higher purity and a better yield. From a suitable fraction of commercial geraniol, two successive separations of the addition compound were sufficient to give substantially pure geraniol. Commercial geraniol of the type used in Japanese beetle bait (*2*), prepared by the fractional distillation under reduced pressure of Java citronella oil, was subjected to steam distillation. The first 75 per cent of the distillate, containing about 40 per cent of geraniol, was used for the preparation of pure geraniol.

In a flask fitted with a mechanical stirrer and reflux condenser, 775 grams of powdered, anhydrous calcium chloride were suspended in 3 liters of hexane by rapid stirring, and 668 grams of the first 75 per cent fraction of commercial geraniol were added. It was found unnecessary to cool the reaction mixture. Stirring was continued for 2 hours, when the mixture was filtered rapidly by suction and the residue washed with three successive 500-ml. portions of hexane. The solid addition product was decomposed by addition to 3 liters of ice water with rapid stirring. The aqueous layer was separated, and the geraniol layer was washed with three successive 500-ml. lots of water and dried over anhydrous sodium sulfate. The dried product was then added to a suspension of 400 grams of calcium chloride in 1500 ml. of hexane and stirred again for 2 hours, and the solid product was separated and decomposed as before. The dried product was freed of hexane under the water pump and then subjected to fractional distillation under reduced pressure (1–2 mm.). The main fraction amounted to 173 grams, $n_D^{25} = 1.4734$. Substantially the same yield was obtained when 5-hour stirring periods were employed.

To obtain a geraniol of higher purity, material that had been through two calcium chloride separations as above was given one additional treatment. This material (580 grams) was added to 1160 grams of calcium chloride in 4 liters of hexane and treated as before. The dried product, after removal of hexane under the water pump, amounted to 538 grams. Under fractional distillation at 1–2 mm. a main fraction was taken of 463 grams, $n_D^{25} = 1.4738$. This was again fractionated at about 0.5 mm. with a longer, 16-inch (40.6-cm.) Vigreaux column. The main fraction (408 grams) had the following properties: $n_D^{25} = 1.4743$; $d^{25} = 0.8751$ gram per cc.; molecular refraction = 49.52 (calculated, 48.86); $[\alpha]_D^{20} = 0.0°$.

Literature Cited

(1) Gildemeister, E., and Hoffman, F., "Die ätherischen Öle", 3rd ed., Vol. I, p. 434 (1928).
(2) Jones, H. A., and Haller, H. L., *News Ed.* (*Am. Chem. Soc.*), 19, 683–5 (1941).
(3) Parry, E. J., "Cyclopaedia of Perfumery", 4th ed., Vol. I, p. 251 (1925).