boiled for five minutes. The reaction was cooled, and the aniline was shaken out with ether and isolated as the hydrochloride. The yield was 0.79 g. or 100% of the theoretical.; m. p. 191°. An excess of phenylhydrazine hydrochloride was added to the alkaline solution, acetic acid was added to slight acidity, and the reaction mixture was allowed to stand for twelve hours. This gave 0.28 g. of the phenylhydrazone of pyruvic acid, or 28%, melting at 186° with decomposition.

The Ethoxyl Derivative III.—Three grams of II was suspended in 75 ml. of absolute alcohol and dry hydrogen chloride was bubbled through the suspension until the dimer dissolved and no further hydrogen chloride was absorbed (about three hours). The alcoholic solution was evaporated to the point of crystallization. The product, white needles from 60% alcohol, melted at 198°. The yield of 1.5 g. or 50% is low due to hydrolytic side reactions since aniline hydrochloride equivalent to 0.75 g. of dimer was isolated.

Anal. Calcd. for $C_{20}H_{20}O_4N_2$: C, 71.42; H, 5.95; N, 8.33. Found: C, 71.04; H, 5.97; N, 8.47.

The Acetyl Derivative IV.—Three-tenths ml. of concentrated sulfuric acid was added to 1.0 g. of II in 10 ml. of boiling acetic anhydride. The reaction was warmed at the boil for one minute then cooled and the acetic anhydride decomposed with dilute caustic. The tarry product recrystallized from 50% alcohol gave 0.7 g. or 70% of small yellow needles melting 148–150°. (The dimer may be crystallized unchanged from boiling acetic anhydride.)

Anal. Calcd. for $C_{20}H_{18}O_4N_2$: C, 71.85; H, 5.38; N, 8.38. Found: C, 71.86; H, 4.88; N, 8.52.

DEPARTMENT OF PATHOLOGY
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RECEIVED MAY 18, 1937

COMMUNICATIONS TO THE EDITOR

SOLANINE-S

Sir:

The alkaloid of *Solanum auriculatum* has been identified as solanine-*s* [Anderson and Briggs, *J. Chem. Soc.*, (in press)] previously isolated only from *S. sodomaeum* [Oddo and Colombano, *Gazz. chim. ital.*, (i), **35**, 27 (1905); Romeo, *ibid.*, (ii), **35**, 579 (1905); Soldaini, *Boll. Chim. Farm.*, **44**, 769, 808, 843 (1905); see also Oddo and Caronna, *Ber.*, **69B**, 283 (1936) and intermediate papers by Oddo and co-workers]. Analyses of this alkaloid and its derivatives now obtained, however, correspond with formulas $C_{44}H_{75}O_{18}N$ and $C_{26}H_{43}O_3N$ for solanine-*s* and solanidine-*s*, respectively, rather than with the formulas $C_{54}H_{96}O_{18}N_2 \cdot H_2O$ and $C_{18}H_{31}ON$ suggested by Oddo. The formula now suggested for solanidine-*s* is supported by the work of Rochelmeyer [*Arch. Pharm.*, **274**, 543 (1936)], who has found that solanidine-*s* yields methylcyclopentenophenanthrene on selenium dehydrogenation, pyrrole bases on zinc dust distillation and a molecular compound with digitonin, thus indicating that solanidine-*s*, like solanidine-*t*, possesses a sterol structure, a fact which does not support Oddo's formula for the aglucone.

Anal. Calcd. for (solanine) $C_{44}H_{75}O_{18}N$: C, 58.34; H, 8.28; N, 1.54. Found: C, 58.38; H, 8.17; N, 2.21, 2.15. Calcd. for (solanidine) $C_{26}H_{43}O_3N$: C, 74.82; H, 10.31; N, 3.35. Found:* C, 74.57, 74.91; H, 10.43, 10.31; N, 3.96, 3.75. Calcd. for $C_{26}H_{43}O_3N \cdot C_6H_3O_7N_3$ (solanidine picrate): C, 59.44; H, 7.12; N, 8.67. Found:* C. 60.18; H, 7.11; N, 8.83.

Recently, Saiyed and Kanga [*Proc. Indian Acad. Sci.*, **4A**, 255 (1936)] have isolated from the fruit of *Solanum xanthocarpum* a glucosidic alkaloid, solancarpine, $C_{44}H_{77}O_{19}N$, hydrolyzed by dilute sulfuric acid to solancarpidine, $C_{26}H_{43}O_3N$, glucose, rhamnose and probably galactose. The formula of solancarpine differs only from that now suggested for solanine-*s* by H_2O while the formula of solancarpidine is the same as that proposed for solanidine-*s*. The melting points of the alkaloids and their derivatives also approximate closely to those already recorded for solanine-*s* and its derivatives and further derivatives now prepared.

It would appear, therefore, from the following comparison of melting points that solancarpine is identical with solanine-*s* or at least that solancarpidine is identical with solanidine-*s*.

The decomposition point of solanine-*s* and those of some of the salts of solanidine-*s* vary consider-

(*) Analyses by Dr. Weiler.

	Solanine-s		Solancarpine	
	Crystal form	M. p., °C.	Crystal farm	M. p., °C.
Gluco-alkaloid	Plates	286 (dec.) (Romeo) 275–280 (dec.) (Oddo)	?	288–289 (dec.)
Agluco-alkaloid	Plates	200 (Oddo) 216–219 (A. and B.)	Plates	197–198
Sulfate	Needles ⟶ plates	? (dec.)	Plates	293–294 (dec.)
Nitrate[a]	Needles	269 (dec.)	Needles	271–272 (dec.)
Hydrochloride	Needles	309.5 (dec.)	Needles	313–314 (dec.)
Hydrobromide	Needles	283 (dec.)	Needles	307–308 (dec.)
Hydriodide[a]	Needles	283–284 (dec.)	Needles	283–284 (dec.)
Picrate	Needles	144–145 (dec.)	Needles	148–149 (dec.)
Oxalate[a]	Needles	238 (dec.)	Needles	238–239 (dec.)
Tartrate[a]	Needles	222 (dec.)	Needles	224–225 (dec.)

(The salts are those of the agluco-alkaloid.) [a] New derivatives.

ably with the rate of heating (in the case of the sulfate by over 100°) which may explain discrepancies in the decomposition points.

DEPARTMENT OF CHEMISTRY L. H. BRIGGS
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RECEIVED MAY 13, 1937

THE PEROXIDE EFFECT IN THE HALOGENATION OF AROMATIC SIDE CHAINS

Sir:

Extensive investigations of bromination of toluene [an extensive literature review of this subject is given by Van der Laan, *Rec. trav. chim.*, **26**, 1 (1907); see also Ref. *a*] indicate that the following factors influence the rate of substitution in the side chain: (1) light, (2) temperature, (3) concentration of bromine, (4) non-metallic catalysts. In an effort to correlate these diverse observations, we undertook an investigation of the effect of peroxides on the bromination of toluene and other aromatic molecules containing side chains. It appeared reasonable that a chain reaction involving bromine atoms might provide a mechanism in harmony with the recorded facts.

We can now state that, as far as brominations in the dark are concerned, peroxides exert a more pronounced effect on the rate of side chain substitution than any of the factors cited above. In this respect our experience with the bromination of toluene is most instructive. In the dark at 25° in the presence of three mole per cent. of ascaridole (on the bromine basis) (other toluene-soluble peroxides are equally effective) the bromination of toluene takes place in about half an hour and the product is over 98% benzyl bromide. Furthermore, the rate of nuclear substitution is increased tremendously by peroxides.

Table I is a summary of some of our results. It is to be noted that the decreased proportion of benzyl bromide in the bromination mixture (as the ratio of toluene to bromine is decreased) is in accord with the postulated bromine atom mechanism.

TABLE I

THE PEROXIDE EFFECT IN THE BROMINATION OF TOLUENE IN THE DARK AT 25°

Moles % Ascaridole	Air	Toluene/Bromine in moles	Reaction time	Monobromide %	Benzyl bromide in product, %	Remarks
3	Present	20	25 min.	85	98	Complete reaction
3	Present	10	1 hour	70	90	HBr evolution ceased
3	Present	5	3 hours	56	30	Incomplete
3	Present	2	3 hours	56	11	Incomplete
None	Present	10	4 days	60	10	Incomplete
None	Absent	10	4 days	56	11	Incomplete
		25	3 weeks	100	36	
None	Present	16	3 weeks	100	20	Complete
None	Present	8	3 weeks	100	10	(Br_2 disappeared)
None	Present	4.7	3 weeks	100	8	

[a] Holleman and Polak, *Rec. trav. chim.*, **27**, 435 (1908).

The reaction of bromine with *p*-chlorotoluene in the presence of peroxides is rather slow at room temperature, but goes to completion in several hours on the water-bath. The product is exclusively *p*-chlorobenzylbromide. Experiments with *o*- and *p*-cyanotoluene at 100° indicate a definite accelerating effect by peroxides.

Examination of the effect of impurities led to the discovery of the remarkable inhibiting effect of very small amounts of alcohols on the rate of bromination in the peroxide catalyzed reaction.

The side-chain chlorination of toluene is accelerated by peroxides.

The study of the effects herein described is being extended to the bromination of aliphatic molecules, and to aromatic compounds containing side chains. A study is also under way to determine whether peroxides will affect the