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PURIFICATION AND CHARACTERIZATION OF PESTICIDAL SYNERGISTS

I. PIPERONYL BUTOXIDE

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SUMMARY

Piperonyl butoxide in greater than 99% purity could be obtained from technical material after a single chromatographic separation on Florisil. Among the identifiable impurities in technical grade material were diethyleneglycol monobutyl ether, dihydrosafrole, 6-methyl dihydrosafrole, 6-propyl piperonyl methoxide, 6-propyl piperonal, 6-chloromethyl dihydrosafrole, 6-propyl piperonylic alcohol, 2-propyl-4,5-dimethoxybenzyl *n*-butyldiethyleneglycol ether, bis(2-propyl-4,5-methylenedioxyphenyl) methane and di(2-propyl-4,5-methylenedioxybenzyl) ether.

INTRODUCTION

Piperonyl butoxide (2-propyl-4,5-methylenedioxybenzyl *n*-butyldiethyleneglycol ether) has been shown to be a potent synergist for pyrethrum[1,2], carbamate[3,4] and chlorinated hydrocarbon insecticide[5,6]. It acts as an inhibitor of the epoxidation of aldrin to dieldrin[7] and dehydrogenation of DDT and hexachloro-cyclohexane[8]. Despite its extensive utility since the early 1940's in such diverse forms as aerosols, wettable powders and dusts and impregnated Kraft liners, the numerous studies describing its involvement with mixed function-oxidases (mfo)[9–12] as well as the varied chromatographic (gas–liquid chromatographic (GLC)[13–19], thin-layer[20–23] and paper[24]) and colorimetric techniques[25–27] utilized for its analysis, no study to date has focused on a detailed elaboration of the components of the technical grade synergist. This information is vital for definitive metabolic, degradation, enzymatic and toxicity studies since the synthetic pathway, *e.g.* reaction of the chloromethyl derivative of dihydrosafrole with the sodium salt of the mono-*n*-butyl ether of dimethylene glycol, yields a technical product of a purity generally in the order of 80% of piperonyl butoxide and 20% of related compounds, some of which may possess synergistic, mfo activity and toxicity *per se*. Thus the major objectives of this study were to delineate chromatographic techniques useful for the preparation of purified piperonyl butoxide

as well as to identify as far as possible the impurities in technical grade samples of synergist utilizing NMR and mass spectrometry (MS) and IR spectroscopy.

EXPERIMENTAL

Sources

Samples of technical grade piperonyl butoxide were obtained from Niagara Chemical Division (Middleport, N.Y.), Hardwicke Chemical Co. (Elgin, S.C.) and Millmaster Chemical Co. (New York, N.Y.), source A, B and C, respectively.

Column chromatography

Columns (Kontes Chromaflex columns K-422230 of 0.5, 12 and 20 mm I.D.); packing: 60–100 mesh Florisil, pH 8.5, activated at 650° (Floridin Co.). This material should undergo no color change on addition of *n*-hexane. For use, the Florisil was hydrated by adding water equivalent to 5% by weight of the dry powder in an air-tight bottle. The mixture was shaken occasionally for a period of at least one week prior to use.

Florisil (1, 10 and 50 g) was packed into the 0.5, 12 and 20 mm I.D. chromatographic columns, respectively, using *n*-hexane as packing solvent. The sample (weight not exceeding 15 mg/g Florisil) was dissolved in 1–2 ml *n*-hexane, applied to the column and the column developed with: (1) *n*-hexane; (2) benzene–*n*-hexane (50:50); (3) benzene–*n*-hexane (90:10); (4) benzene–diethyl ether (95:5); and (5) methylene chloride–glacial acetic acid (95:5) (all solvent volumes were 5 ml/g Florisil). The flow rate was approximately 4 ml/min per centimetre column diameter.

All solvents were concentrated by water aspiration, the sample weighed, and eluents (1), (2), (3) and (4) brought to about 1% concentration in *n*-hexane, while eluent (5) was dissolved in methanol to a 1% concentration, for subsequent GLC and/or thin-layer chromatographic (TLC) analysis.

Adsorptive chromatography

In order to prepare a concentrate of those impurities less polar than piperonyl butoxide, a benzene–Florisil (unhydrated) (500 ml:200 g) mixture was prepared to which 3 g of technical grade piperonyl butoxide was added and the mixture was allowed to stand 15–20 h with occasional shaking. The benzene was removed by gravity filtration and the Florisil washed with two 250-ml benzene aliquots and filtered. The solvents were pooled and removed with a water–vacuum flash evaporator.

The remaining sample was taken up in 1–2 ml *n*-hexane and applied to a 12-mm I.D. chromatographic column containing hydrated (5%) Florisil in *n*-hexane. The column was sequentially developed with 70 ml of each of the following solvents: (1) *n*-hexane; (2) *n*-hexane–benzene (75:25); (3) *n*-hexane–benzene (50:50); (4) *n*-hexane–benzene (25:75); (5) benzene; and (6) benzene–ethyl ether (95:5). All eluate fractions were monitored by TLC (10 μl sample per solvent fraction) by spraying the developed plate with chromotropic acid.

Thin-layer chromatography

Silica Gel GF (250 μ, Analtech) plates were initially washed with chloroform–methanol (1:1) by ascending development, the solvent evaporated at room temper-

ature (5–10 min) and the plates activated at 110–120° for 30 min. Samples (10–25 μl) were applied with a repeating dispenser (Applied Science PB600) or with a sample streaker (Applied Science) and developed with benzene–acetone (95:5) to a distance of 150 mm in a lined tank. Detection was achieved with (a) 10% w/v aq. solution of sodium 1,8-dihydroxynaphthalene-3,6-disulfonate (chromotropic acid). One volume of this solution was mixed with five volumes of a conc. sulfuric acid–water (5:3) solution. (The acid–water solution must be allowed to cool to room temperature before mixing with the naphthalene salt.) The reagent was then sprayed on the plate, and the plate heated to 120° for 5–15 min for spot color development; (b) spraying with a saturated solution of phosphomolybdic acid in 95% ethanol, heating to 110° for 5–10 min; (c) compounds that absorbed under shortwave were detected as a quench on the fluorescent TLC plates.

Preparative thin-layer chromatography

Multi-component eluent samples from the Florisil columns were separated on Silica Gel GF plates (Analtech). Approximately 5–8 mg samples, 1% solutions in *n*-hexane or methanol, were streaked across each plate at the origin, then developed as described above for TLC. Resolved components were located on the plates as quenched spots, then removed by vacuum with a 2-ml Chromaflex sample recovery tube (Kontes); the sample was then eluted from the silica gel with acetone/ether from the sample recovery tube or from a 10–15 ml sintered glass funnel. The solvent was removed under vacuum and approximately 1 ml of *n*-hexane was added to the TLC-separated components for subsequent analysis.

Gas chromatography

Hewlett-Packard Model 5750 and Varian Aerograph Model 1200 gas chromatographs with 1 mV recorders and hydrogen flame ionization detectors were used in these studies. Samples were analyzed on 3.5 m × 2 mm I.D. stainless-steel columns packed with (1) 10% OV-17 on 80–100 mesh Supelcoport or (2) 10% OV-225 on 80–100 mesh Supelcoport. Helium carrier gas flow rate was 35–40 ml/min, injection ports were maintained at 260°, and detector blocks at 290°. The OV-17 columns were linearly programmed between 200° and 280° at 10°/min, and the OV-225 from 160° to 260° at 8°/min.

The chromatograms obtained using OV-17 were compressed relative to those from OV-225; furthermore, catechols were eluted from OV-17 without silylation. For these reasons, compounds or zones from the preparative thin-layer plates were examined routinely on the OV-17 column. Resolution of similar compounds was greater on OV-225, which therefore was used for all quantitative analyses reported here.

Quantitative measurements were made in terms of peak areas (height times width at half-height) relative to an internal standard of *n*-dotriacontane. Relative peak areas were then corrected for relative weight responses determined for pure components either synthesized or isolated from commercial piperonyl butoxide by column chromatographic (CC) and TLC methods described above. All quantitative measurements reported here are averages of 3–6 determinations and have relative standard deviations of $\pm 5\%$.

Commercial samples of piperonyl butoxide were chromatographed both as 1%

solutions in methylene chloride, and without added solvent to detect low-boiling material that would otherwise be lost in a solvent peak.

GC–MS was accomplished using a Perkin-Elmer Model 270 instrument. Samples were introduced through a 1 m × 2 mm column packed with 3% Dexil 300 on Gas-Chrom Q at various temperatures. Usually the samples were previously purified by preparative TLC such that the much greater separating power of OV-225 was not needed. Spectra were obtained with an ionization potential of 70 eV, and molecular ions confirmed at 35 eV.

Other analytical methods

IR spectra were taken of thin films on salt plates using a Perkin-Elmer Model 621 instrument. Samples were subjected to both IR and NMR examination only after GLC on both OV-17 and OV-225 indicated that a single component was present.

NMR spectra were scanned in $CDCl_3$ containing 1% tetramethylsilane (0 p.p.m.) as internal reference, using a Varian T-60 spectrometer.

Reference compounds

6-Chloromethyl dihydrosafrole, 6-propyl piperonal, and 6-propyl piperonyl methoxide were obtained from Hardwicke Chemical Co. Dihydrosafrole and 1,2-methylenedioxybenzene were from Frinton Laboratories (S. Vineland, N.J.) Butyl carbitol (diethyleneglycol monobutyl ether) was from J. T. Baker Chemical Co. 6-Propyl piperonylic alcohol was synthesized by reducing the corresponding aldehyde with sodium borohydride in 95% ethanol. *n*-Dotriacontane was from Analabs, Inc.

RESULTS AND DISCUSSION

The chromatographic procedures

Table I summarizes the GLC-resolvable components of the five Florisil column fractions. To distinguish all twenty-five of the GLC peaks in Table I it was necessary to apply a preliminary subfractionation and concentration by preparative TLC. In general, the components migrating more slowly than piperonyl butoxide on TLC were purified by TLC of Florisil column fraction 5; the components moving ahead of piperonyl butoxide on Silica Gel GF were more readily purified by TLC of the benzene phase of the benzene–Florisil batch process. None of the peaks listed in Table I were observed when Florisil–Silica Gel GF procedural blanks were examined.

The recovery of 99% pure piperonyl butoxide in Florisil fraction 4 averaged 91.3 ± 3.8 (S.D.)% of that present in the three commercial preparations. The degree of purification achieved can be judged by examination of lane 4 in Fig. 1 (TLC) and of Fig. 2 (GLC); quantitative determination of purity was accomplished by GLC on OV-225 with internal standard.

Purification of piperonyl butoxide on Florisil gives a colorless product; we have not been able to achieve comparable purification with silicic acid columns alone. Preparative TLC[28] yields an adequately pure product, but is extremely tedious when gram quantities of pure piperonyl butoxide are required.

GLC methods presently in the literature[15,17,19] for the quantitative analysis of piperonyl butoxide inevitably, in our hands, indicated higher purities for commercial piperonyl butoxide preparations than did analysis on OV-225. Most commonly, the

difficulty could be traced to including the dimethoxybenzene analog of piperonyl butoxide in the piperonyl butoxide value when columns less polar than OV-225 were used.

TABLE I

CORRELATIONS BETWEEN GLC, TLC AND COLUMN FRACTIONS OF COMMERCIAL PIPERONYL BUTOXIDES

GLC on 3.5 m × 2 mm I.D. s.s. columns of 10% OV-17 on 80–100 mesh Supelcoport; 200–280° at 10°/min; helium, 35–40 ml/min; 5 mm/min chart.
CC on hydrated (5%) Florisil, 60–100 mesh. Fraction (1) *n*-hexane; (2) benzene–*n*-hexane (50:50); (3) benzene–*n*-hexane (90:10); (4) benzene–diethyl ether (95:5); (5) methylene chloride–glacial acetic acid (95:5).
TLC on Silica Gel GF plate; development with benzene–acetone (95:5) in a lined tank (to 150 mm).

GLC peak	*GLC Rd' (cm)*	*Column fraction*	*TLC R_F*	*Comments*
1	0.40	5	0.05	Butyl carbitol
2	0.55	1	0.75	Dihydrosafrole
3	0.81	1	0.75	6-Methyl dihydrosafrole
4	1.08	2–3		Absent from source C
5	1.50	2	0.60	6-Propyl piperonyl methoxide
6	1.60	2	0.58	6-Propyl piperonal
7	1.71	3	0.55	6-Chloromethyl dihydrosafrole
8	1.85	3	0.24	6-Propyl piperonylic alcohol
9	2.16	1	0.79	Methylenedioxy absent; source A only
10	2.80	2	0.60	Methylenedioxy absent
11	3.15	5	0.10	Absent from source C
12	3.30	5	0.06	Mol. wt. 218
13	3.42	2	0.58	Source A only
14	3.72	5	0.15	Methylenedioxy present
15	4.12	4	0.41	Significant in source B only
16	4.23	4	0.24	Methylenedioxy absent
17	4.70	3–5	0.40	Source A only
18	4.90	2	0.59	Methylenedioxy absent
19	5.08	3–5	0.37	Piperonyl butoxide
20	5.20	5	0.18	2-Propyl-4,5-dimethoxybenzyl *n*-butyl-diethyleneglycol ether
21	5.40	2–5		Possibly GLC breakdown product
22	6.40	4	0.40	Absent from source C
23	7.60	2	0.58	Source A only
24	8.10	2	0.73	Bis[2-propyl-4,5-methylenedioxyphenyl] methane
25	11.7	2	0.70	Di[2-propyl-4,5-methylenedioxybenzyl] ether

When both a high degree of purification and a high recovery of piperonyl butoxide were desired, we found it helpful to monitor the column fractionation during the elution of fraction 3 (benzene–*n*-hexane, 90:10). Drops of eluate were caught on microscope slides coated with Silica Gel GF and developed in less than 5 min in a Coplin staining jar containing benzene–acetone (95:5). The elutant applied to the Florisil column was changed to benzene–ether (95:5) as soon as piperonyl butoxide was detected on a micro-TLC plate. This procedure also compensates for any variation in batches of Florisil.

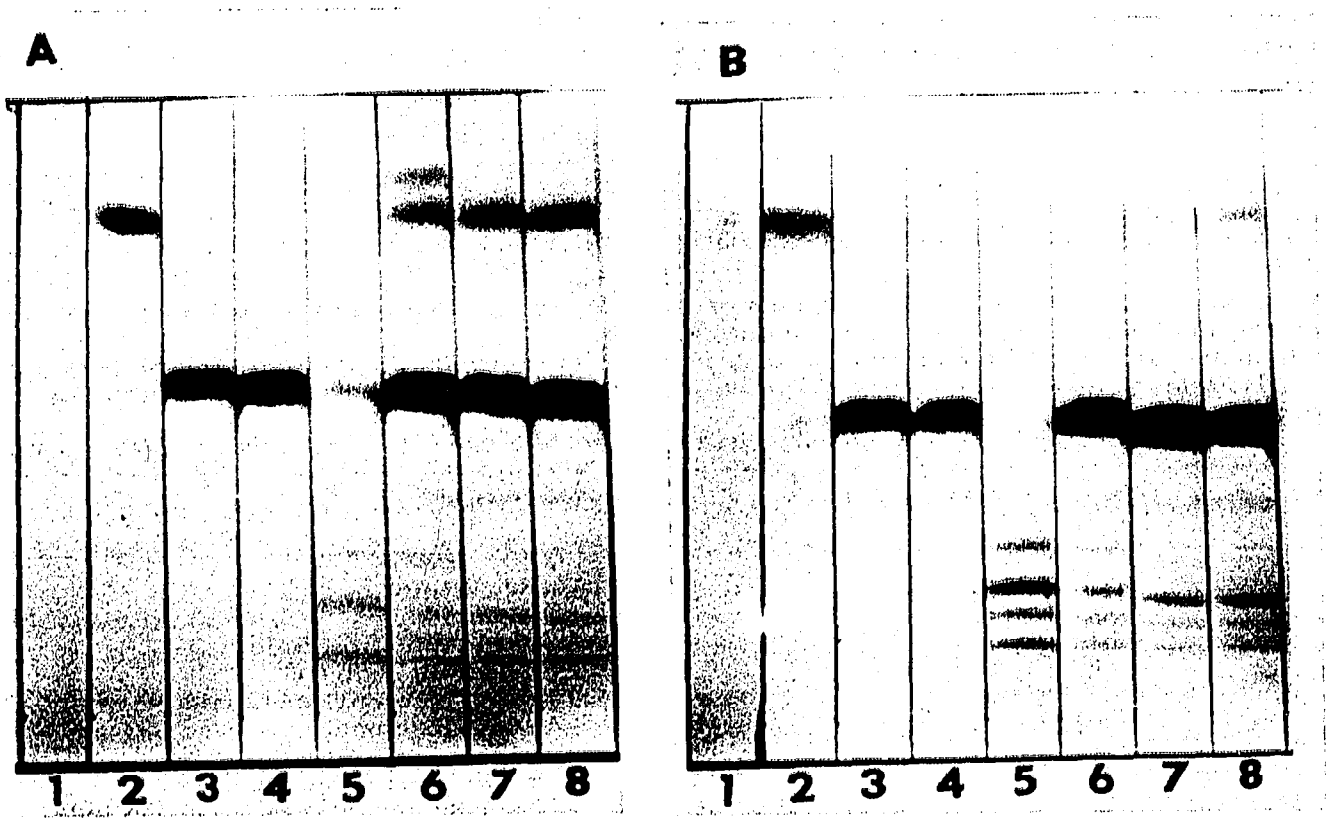


Fig. 1. TLC of sources A, B, C on 250 μ Silica Gel GF plates, lined tank, in benzene–acetone (95:5). Spots visualized with saturated ethanolic phosphomolybdic acid in (A), chromatrophic acid in (B). Lanes represent: (1) Florisil fraction 1, source A; (2) Florisil fraction 2, source A; (3) Florisil fraction 3, source A; (4) Florisil fraction 4, source A; (5) Florisil fraction 5, source A; (6) unfractionated piperonyl butoxide, source A; (7) unfractionated piperonyl butoxide, source B; (8) unfractionated piperonyl butoxide, source C.

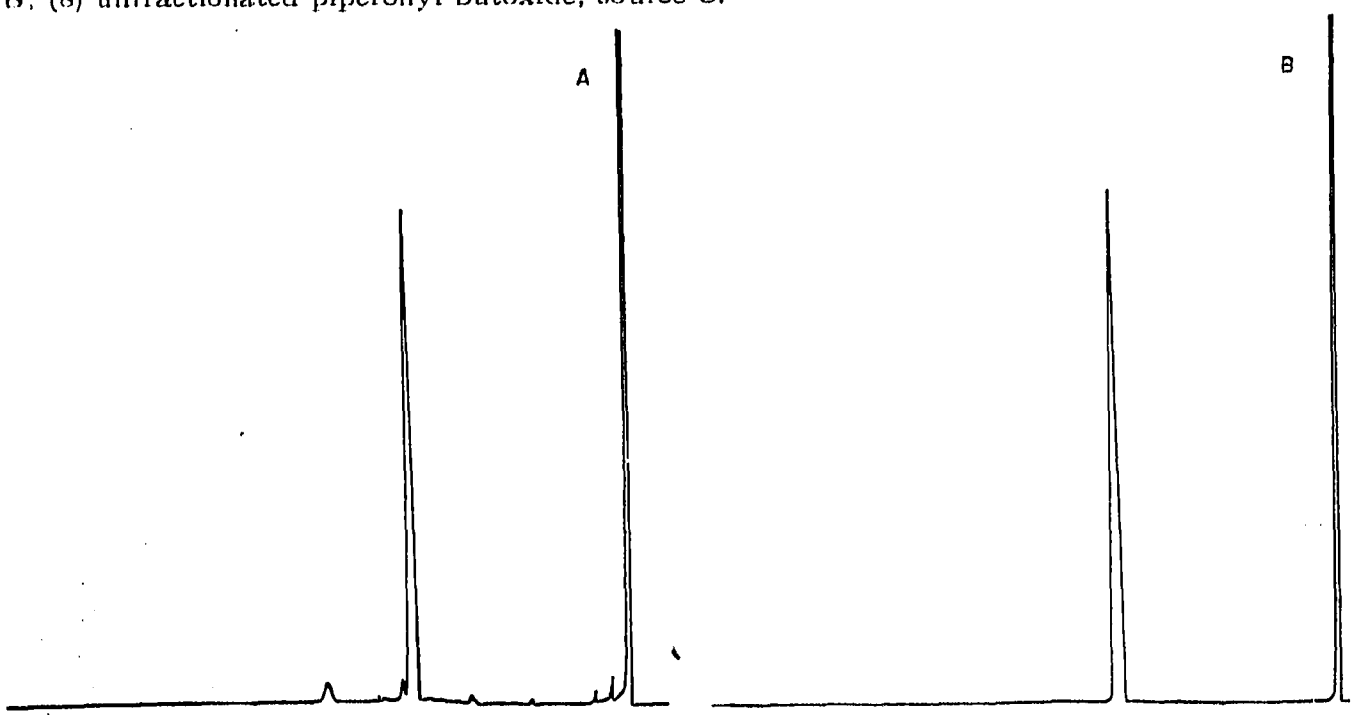
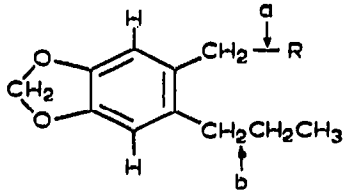


Fig. 2. GLC of source A on OV-225, conditions described in text. (A) = Unfractionated piperonyl butoxide; (B) = Florisil fraction 4.

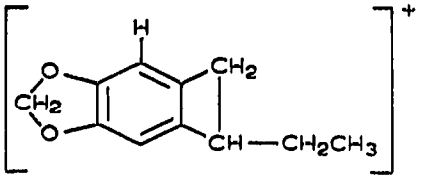
Identification of major components

Infrared spectra. The compounds, for which IR spectra were run, include all those listed in Table II (mass spectra) except compound 12, which could not be sufficiently purified by TLC. Of these, only butyl carbitol showed –OH absorption (2.9 μ), and none showed C=O between 5.6 and 6.1μ. All except butyl carbitol showed the aromatic ring by absorption at 6.2 μ and near 14–15 μ; all showed the methylenedioxy ring at 1255 cm^{-1} except butyl carbitol and compound 20, the latter having $\geqslant$–OCH_3 very strong at 1109 cm^{-1}. The methylenedioxyphenyl group also gives rise to a characteristic absorption peak for $-CH_2-O-\dot{C}=\dot{C}-$ at 1037 cm^{-1}. An "isolated" propyl group absorption at 760 cm^{-1} was seen in all cases except for butyl carbitol. The aliphatic ether groups in the butoxy (ethoxy) ethoxy side-chain show up as intense absorption around 1100 cm^{-1}; the ether group is at 1090 cm^{-1} in the case of propyl piperonyl methoxide. The 1100-cm^{-1} peak was absent in the case of dihydrosafrole, 6-methyl dihydrosafrole, compound 24 and compound 25.

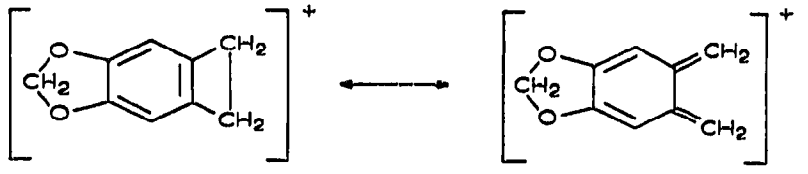
Mass spectra. All those compounds having the general structure 2-propyl-4,5-methylenedioxybenzyl:



show a molecular ion, and a base peak at either *m/e* 176 or *m/e* 149. The peak at *m/e* 176 is attributed to the rearrangment ion resulting from cleavage at "a" above with loss of a hydride ion to give:



The peak at *m/e* 149 is tentatively attributed to the resonance forms:



resulting from concerted cleavage at "a" and "b" above. Replacement of a methylenedioxy group by two methoxy groups results in mass spectra essentially identical except that the major peaks in the latter are displaced 16 units toward higher mass values. Presence of a butoxy (ethoxy) ethoxy side-chain is revealed by a series of peaks at *m/e* 57, 75, 87, 101, 119, 131, 145 and 163, all of which should be present. In particular, absence of a significant peak at *m/e* 57 seems to be presumptive evidence for the absence of the butoxy (ethoxy) ethoxy side-chain.

Presence of the propyl side-chain is indicated by the occurrence of ions at

TABLE II

MASS SPECTRAL DATA OF IMPURITIES IN COMMERCIAL PIPERONYL BUTOXIDE

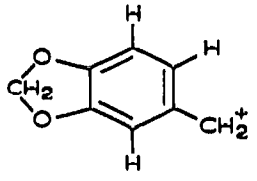
Compound[a]	*m/e values*		*Abundance relative to compound of lowest base peak, m/e 57*	*m/e 29 and m/e 43 present; m/e 57 absent?*	*m/e values and relative abundance of other ions relevant to characterization of the compound*
	Molecular ion (M^+ peak)	*Base peak*			
Dihydrosafrole	164	135	<1	yes	148 (1.2%), 105 (8.9%)
Compound 3	178	149	<1	yes	119 (6.0%)
6-Propyl piperonyl methoxide	208	176	<1	yes	149 (9.5%), 165 (3.4%)
Piperonyl butoxide	338	176	26	yes	119 (11.1%), 149 (25.4%)
Compound 12	218	57	100	no	103 (49%), 119 (10%), 145 (5%)
Compound 20	354	192	76	yes	165 (85%), 177 (22%)
Compound 24	340	176	<1	yes	149 (7%)
Compound 25	384	149	<1	yes	135 (62%), 176 (82%), 369 (15%)
Butyl carbitol	162	57	100	no	144 (0.9%), 132 (2.3%)

[a] Named compounds represent those whose mass spectra could be compared to those of known standards; the numbers of the compounds represent the GLC peaks, column 1 of Table I.

m/e 29 and *m/e* 43 with *m/e* 57 being absent, and all of the compounds in Table II showed this except compound 12 and butyl carbitol.

The two compounds found lacking butoxy (ethoxy) ethoxy side-chains, yet having molecular weights above that of piperonyl butoxide had no uniquely distinctive major ions. The spectrum of compound 24 had no peaks greater than 10% in relative abundance above *m/e* 100 other than its base peak of *m/e* 176. Accordingly, the identification of this component rested largely on application of its apparent molecular weight of 340 to the NMR and IR spectra.

Compound 25, the highest molecular weight component observed, had major peaks at both *m/e* 149 and *m/e* 176 (discussed previously), and a major peak at *m/e* 135 tentatively attributed to:



Again, the identification of this component rested largely on its molecular weight, NMR and IR spectra.

The named compounds in Table II represent those whose mass spectra could be compared to those of known standards.

Summary of characteristics (See Tables II–IV)

The following compounds isolated from commercial piperonyl butoxide could be characterized by direct comparison of their IR, NMR and mass spectra and GLC retention times with those of the corresponding commercially available standards: piperonyl butoxide itself, dihydrosafrole, 6-propyl piperonyl methoxide, and butyl carbitol.

TABLE III

NMR SPECTRA OF IMPURITIES IN COMMERCIAL PIPERONYL BUTOXIDE

p.p.m.	*Type*	*Compounds*					
		Piperonyl butoxide	*Compound 3*	*6-Propyl piperonyl methoxide*	*Compound 20*	*Compound 24*	*Compound 25*
0.9	triplet	6	3	3	6	6	6
1.5	multiplet	6	2	2	6	4	4
2.2	singlet	0	3	0	0	0	0
2.5	triplet	2	2	2	2	4	4
3.3	singlet	0	0	3	0	0	0
3.4	triplet	2	0	0	2	0	4
3.6	triplet	8	0	0	8	0	0
3.8	singlet	0	0	0	0	2	0
3.9	singlet	0	0	0	6	0	0
4.45	singlet	2	0	2	2	0	0
5.85	singlet	2	2	2	0	4	4
ca. 6.6	singlet	1	2	1	1	2	2
ca. 6.8	singlet	1	0	1	1	2	2

TABLE IV

ASSIGNMENT OF NMR PEAKS

p.p.m.	*Structure*
0.9	C(satd.)–CH_3
1.5	C(satd.)–CH_2–C(satd.)
2.2	Ar–CH_3
2.5	Ar–CH_2–CH_2–
3.3	C(satd.)–O–CH_3
3.4	C(satd.)–CH_2–CH_3–O
3.6	O–CH_2–CH_3–O–
3.8	Ar–CH_2–Ar
3.9	Ar–O–CH_3
4.45	Ar–CH_3–O
5.85	O–CH_2–O
ca. 6.6 and *ca.* 6.8	Ar–H

The following compounds were not isolated in pure form and were tentatively identified by co-GLC with the corresponding standards on Dexsil 300, OV-17 and OV-225 : 6-propyl piperonylic alcohol (also by GLC of trimethylsilyl ether derivatives), 6-chloromethyl dihydrosafrole, and 6-propyl piperonal.

Compound 3, (6-methyl dihydrosafrole). (a) IR Data. Aromaticity present, methylenedioxy group present, aliphatic ether side-chain absent, –OH and C=O absent, propyl side-chain indicated.

(b) Mass spectrum. Similar to that of dihydrosafrole but mol. wt. 178. Confirms absence of butoxy group and presence of propyl side-chain.

(c) NMR spectrum. Confirms dihydrosafrole organization and identifies the additional mass as 6-methyl group.

Compound 20, (2-propyl-4,5-dimethoxybenzyl n-butyldiethyleneglycol ether). (a) IR data. Methoxyphenyl indicated, methylenedioxy absent, aliphatic ether probable, no –OH or C=O, probably propyl side-chain.

(b) Mass spectrum. Similar to that of piperonyl butoxide except shifted 16 mass units higher.

(c) NMR spectrum. Same as piperonyl butoxide except methylenedioxy absent, two methoxy groups indicated instead.

Compound 24, (bis[2-propyl-4,5-methylenedioxyphenyl] methane). (a) IR data. Very similar but not identical to 6-methyl dihydrosafrole.

(b) Mass spectrum. Mol. wt. 340, no butoxy group. Propyl side-chain. Base peak indicates the basic dihydrosafrole organization. Absence of major fragments between base peak and molecular ion suggests dimer-like structure.

(c) NMR spectrum. Same as dihydrosafrole with "1/2" a CH_2 group attached to benzene ring, confirms dimer-like structure through a single –CH_2-bridge.

(d) Synthesis. This compound was synthesized by an established procedure[29,30] and matched with the unknown in all parameters discussed.

Compound 25, (di[2-propyl-4,5-methylenedioxybenzyl]ether). (a) IR data. Methylenedioxyphenyl, propyl side-chain, and aliphatic ether present; –OH and C=O absent.

(b) Mass spectrum. Mol. wt. 384. Base peak *m/e* 149 with *m/e* 176 and *m/e* 135 very high indicated dihydrosafrole organization with carbon substituted at C-6. No butoxy group.

(c) NMR spectrum. Same as 6-propyl piperonyl methoxide except $-CH_2-O-$ instead of CH_3-O. Minimum proton per functional group count gave half the known molecular weight (on total group basis), indicating symmetry. Doubling the number of each group indicated gave agreement with known nolecular weight and structure named above. Final structure postulated above is in agreement with GLC and TLC migrations relative to those of compound 24.

Compound 12, (unknown). (a) Mass spectrum. Mol.wt. 218, 57 units higher than butyl carbityl group. Fragmentation pattern consistent with butyl carbityl part structure.

TABLE V

COMPOSITION OF COMMERCIAL PIPERONYL BUTOXIDES

Sources of the samples are described in text.

Compound	*Weight %*[a]		
	Source A	*Source B*	*Source C*
Piperonyl butoxide	71.6	90.1	80.6
Butyl carbitol	3.2	3.5	0.6
Bis(2-propyl-4,5-methylenedioxyphenyl) methane	2.7	3.5	6.4
2-Propyl-4,5-dimethoxybenzyl *n*-butyl diethyleneglycol ether	2.3	0.5	0.4
Di(2-propyl-4,5-methylenedioxybenzyl) ether	0.3	1.0	0.3
6-Propyl piperonylic alcohol	<0.1	<0.1	<0.1
6-Chloromethyl dihydrosafrole	≪0.1	≪0.1	≪0.1
Dihydrosafrole	≪0.1	<0.1	≪0.1
Compound 14[b]	0.8	0.6	0.9
6-Propyl piperonal	0.2	≪0.1	<0.1
6-Propyl piperonyl methoxide	<0.1	<0.1	<0.1
6-Methyl dihydrosafrole	<0.1	<0.1	<0.1
"Low boilers"[c]	7.0	<0.1	0.6
Phenols, catechols, acids[d]	0.9	≪0.1	0.3
Unaccounted for[e]	8.4	0.4	8.4

[a] Based on GLC. Relative S.D.: + 5%.
[b] Compound 14 represents GLC peak No. 14, see Table I.
[c] Elute from gas chromatograph before butyl carbitol.
[d] Extractable from ether solution of piperonyl butoxide into 1 *N* aq. NaOH.
[e] Includes polymers and unidentified gas chromatographable material.

(b) IR, NMR. This compound could not be separated from 3 other components of its TLC band except by GLC, so these spectra were not run.

(c) Chromatographic evidence. This compound moves in the second band above the origin on TLC, indicating high polarity. It does not react with silylating reagents according to GLC before and after attempted derivatization.

A summary of the analyses of the three commercial preparations of piperonyl butoxide is given in Table V.

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