[Contribution from the Chemistry Department of the University of Queensland]

A Re-Examination of Indian and Loblolly Turpentines

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A re-examination of *Pinus longifolia* turpentine has revealed the additional constituents α-thujene, myrcene, limonene, and terpinolene. Additional constituents recognized in *Pinus taeda* turpentine are myrcene, *p*-cymene, limonene, and methyl chavicol. β-Carene was not detected in either turpentine.

Pseudo- or β-carene, a likely constituent of essential oils on biogenetic grounds, has not yet been isolated although it has been suggested as a constituent of *Pinus sylvestris*,[1,2] *Pinus longifolia*,[3,4] and *Pinus taeda*[5] turpentines. In no case has β-carene been obtained as a major component of a fraction or concentrate nor has it been adequately characterized by derivatives or degradation products.[6]

Some physical properties of β-carene have been approximately predicted[5] by consideration of regularities associated with exocyclic double bonds, the anticipated values being b.p. *ca.* 70–75° (20 mm.), n_D^{25} *ca.* 1.480, and d_4^{25} *ca.* 0.870. With this guide, we have re-examined samples of *P. taeda* and *P. longifolia* turpentines using efficient stills and the sensitive refractive index-density chart[5,7] for the detection of minor components.

Loblolly turpentine. This turpentine from *P. taeda* has been previously examined by Mirov, Wang, and Haagen-Smit[8] who identified (+)α-pinene (85%) and (−)β-pinene (12%). The properties of the distillation fractions reported by Mirov, *et al.*, when plotted on the refractive index-density chart (see Fig. 1) led one of us to suggest[5] that β-carene might be a constituent of the turpentine. Through the kind intervention of Dr. N. T. Mirov a further sample which closely resembled in physical constants that examined by Mirov, *et al.*, was obtained.

Our examination of this sample confirmed the predominance of α-pinene (71%) and β-pinene (22%) but the refractive index-density curve (Fig. 1) did not reproduce that drawn from the data of Mirov, *et al.*, and no indication of the presence of β-carene was found. However in addition to the two pinenes, myrcene, limonene, and *p*-cymene were identified (the latter by ultraviolet absorption only) and together totalled about 1% of the turpentine. Methyl chavicol comprised a further *ca.* 1% of the turpentine, unidentified sesquiterpenes about 1%, and an unidentified α,β-unsaturated ketone of b.p. 88° (10 mm.) perhaps $^1/_2$%. Other unidentified substances amounted to a further 3–4%.

The *n-d* curve of Mirov's sample shows the presence of a substance easily separated from α-pinene by its higher volatility and having a higher density but lower refractive index than α-pinene. This is suggestive of the presence of tricyclene but in our sample traces only of the substance were detected by the slightly displaced position of the points for the first two fractions. Other minor constituents were revealed in fraction 26 by a maximum ($[\alpha]_D$ −3.3°) in the optical rotation and in fractions 27 and 28 by a convexity preceeding the approach to *cis*-decalin in fraction 29.

New derivatives for the characterization of α- and β-pinene were prepared in the S-benzylthiuronium salts of the peroxide-catalysed adducts of thioglycollic acid and the respective terpenes. The derivatives, prepared easily in good yield, exhibit the same disadvantages as the corresponding derivatives of acyclic olefins.[9]

Indian turpentine. The refractive index-density curve of the fractionated *P. longifolia* turpentine (see Fig. III of ref. 5) confirms the presence of the previously reported[10] constituents α-pinene, β-pinene, and 3-carene. The terpenes, limonene (previously suspected as a constituent),[10] α-thujene, myrcene, and terpinolene, indicated as constituents by inspection of the *n-d* curve, have now been confirmed by the preparation of derivatives. Fraction 31, (see ref. 5) the boiling range of which approximated the boiling point predicted for β-carene, was ozonized but yielded no steam-volatile carbonyl compound[6] derived from β-carene. There is thus no evidence to suggest the presence of β-carene in this sample of Indian turpentine.

A synthesis of β-carene is being attempted.

EXPERIMENTAL

Loblolly turpentine. A sample of oleoresin from *Pinus taeda* kindly supplied by Mr. W. Langdale of Florida, U.S.A.

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(1) Semmler and von Schiller, *Ber.*, **20,** 1591 (1927).

(2) Rudakov and Antamanov, *J. Gen. Chem. U.S.S.R.*, **15,** 75 (1945).

(3) Joffree, *Bull. inst. pin.*, **79,** 109 (1931).

(4) Dupont and Joffre, *Chimie & industrie*, Special No. 641 (March, 1932).

(5) Sutherland, *Perfumery and Essent. Oil Record*, **43,** 453 (1952).

(6) Elsevier's *Encyclopaedia of Organic Chemistry*, Vol. **12A,** 1948, p. 35.

(7) Mirov, Wang, and Haagen-Smit, *J. Am. Pharm. Assoc.*, **38,** 403 (1949).

(8) Sutherland, *Univ. Queensland Papers, Chem. Dept. I,* No. 34 (1948).

(9) Sutherland, *J. Am. Chem. Soc.*, **75,** 5947 (1953).

(10) Simonsen, *J. Chem. Soc.*, **117,** 570 (1920).

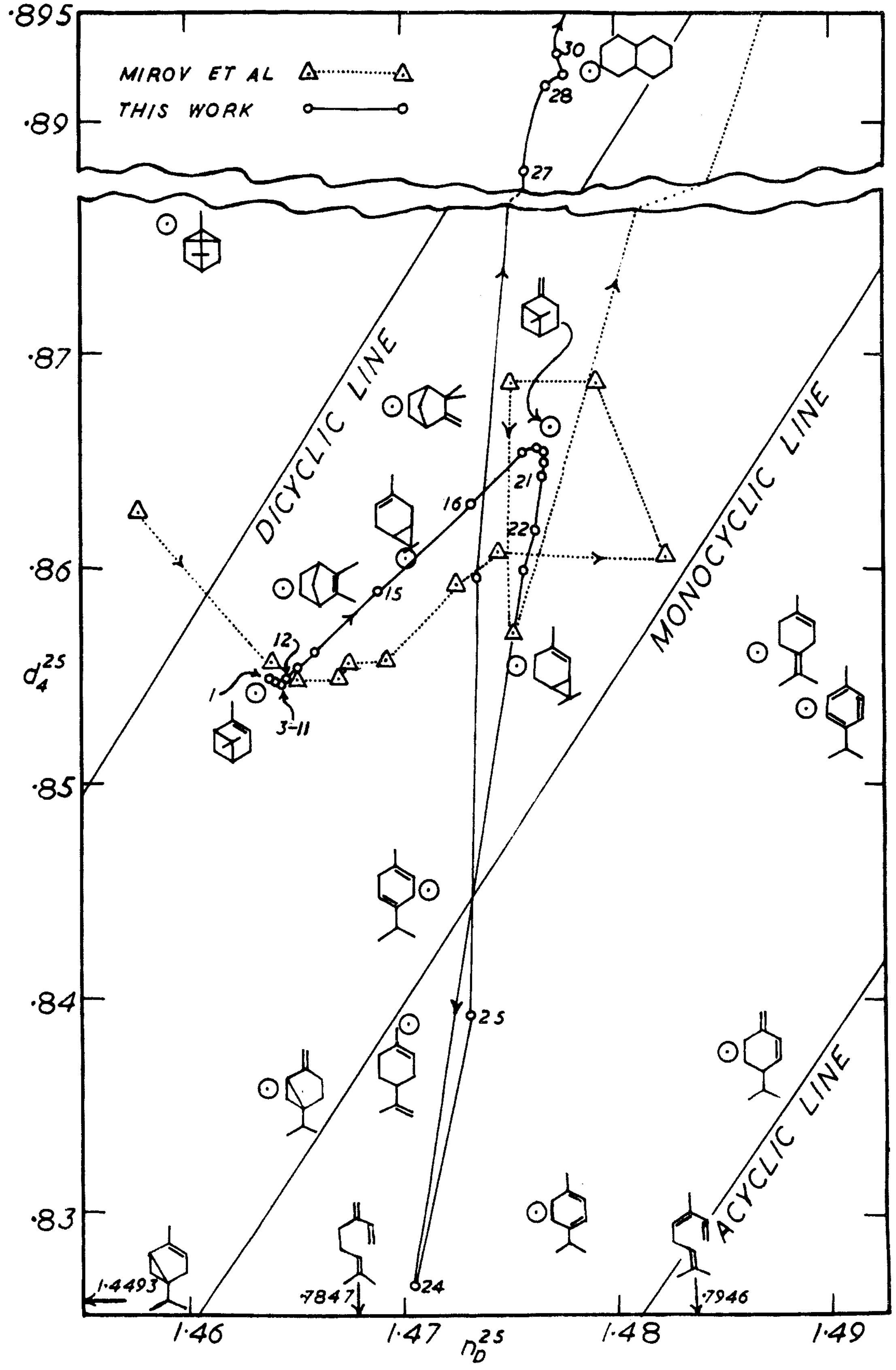
·895
·89
·87
·86
·85
·84
·83
d_4^{25}
MIROV ET AL
THIS WORK
DICYCLIC LINE
MONOCYCLIC LINE
ACYCLIC LINE
30
28
27
16
15
12
1
3–11
21
22
25
24
1·4493
·7847
·7946
1·46
1·47
1·48
1·49
n_D^{25}

Fig. 1

was partially lost in transit through damage to the container. The 2817 g. of oleoresin on steam distillation yielded 390 ml. of oil of constants d_4^{25} 0.8592, n_D^{25} 1.4683, and $[\alpha]_D$ +24.1°. A further 65 ml. of similar oil was recovered from the resin-contaminated wrappings of the container.

The combined oils (425 ml.) were fractionated at 20 mm. in a 20 inch Lecky Ewell still with reflux ratio 12 to fraction 22 inclusive, when the boiling point just exceeded that of β-pinene. The residue (32.5 ml.) to which was added *cis*-decalin (15 ml.) as chaser, was cut into 16 fractions at 10 mm. pressure in a one-metre Bower Cooke type still at reflux ratio 30.

(+)*α-Pinene.* Fractions 2 [b.p. 52.5–52.7° (10 mm.), n_D^{25} 1.4639, d_4^{25} 0.8546, $[\alpha]_D^{29}$ +38.3°] to 12 correspond very closely in physical properties to α-pinene and fraction 2 oxidized by Delepine's method,[11] yielded a mixture of racemic pinonic acid, m.p. 104–105°, and active pinonic acid, m.p. 62–64°.

Thioglycollic acid adduct of α-pinene. Fraction 7 (1 ml.) and freshly distilled thioglycollic acid (2 ml.) were shaken with a small drop of ascaridole until homogeneous (4 hours) and allowed to stand a further 24 hours. The reaction mixture in ether was extracted with water until free from thioglycollic acid and then titrated with 1.75 *N* NaOH (Bromothymol Blue). The aqueous layer was run into an aqueous solution of an equivalent amount of S-benzylthiuronium chloride and the precipitated salt was washed with cold acetone to remove the adsorbed indicator and dried to give 2.02 g. (83% yield) of the crude salt, m.p. 158–159°. After several crystallizations from acetone-methanol (2:1) colorless needles, m.p. 161–162° (immersed at 150°), $[\alpha]_D^{24}$ −20.5° (*c*, 0.68 in MeOH) were obtained.

Anal. Calc'd for $C_{20}H_{30}N_2O_2S_2$: C, 60.85; H, 7.66; N, 7.10. Found: C, 60.6; H, 7.77; N, 7.13.

(−)*β-Pinene.* Fractions 18 to 20 correspond very closely in physical properties with β-pinene. The fractions 13 to 17 lie on the straight line between the points for α and β-pinenes in the *n-d* chart and hence show the absence of camphene.[5]

Fraction 20 [b.p. 59.9° (20 mm.) n_D^{25} 1.4766, d_4^{25} 0.8649 $[\alpha]_D$ −19.9°] ozonized in 85% acetic acid at 0° and worked up with a zinc dust reduction gave a 50% yield of crude nopinone from which the characteristic semicarbazone, m.p. 185°, and 2,4-dinitrophenylhydrazone,[12] m.p. 145–146°, were prepared.

Thioglycollic acid adduct of β-pinene. A procedure similar to that used for the α-pinene adduct gave an 83% yield of crude salt of m.p. 157°. Several crystallizations from acetone-methanol gave colorless needles, m.p. 156.6–157.5° (immersed at 150°), $[\alpha]_D^{22°}$ −16.5° (*c*, 1.56 in MeOH).

Anal. Calc'd for $C_{20}H_{30}N_2O_2S_2$: C, 60.85; H, 7.66; N, 7.10. Found: C, 60.9; H, 7.66; N, 7.12.

Mixtures of the α-pinene and β-pinene derivatives show little or no depression of melting point below that of the β-pinene salt.

Myrcene. The physical properties of fraction 24 [1 ml., b.p. 63–70° (20 mm.) d_4^{25} 0.8265, n_D^{25} 1.4705, $[\alpha]_D^{25}$ −4.4°, $\epsilon_{max.}$ = 7100 at 226 *mμ*] suggested the presence of about 40% of myrcene, taking $\epsilon_{max.}$ for pure myrcene[13] as 1.84 × 10^4 at 224.5 mμ. Refluxing with maleic anhydride in toluene for one hour and subsequent hydrolysis, yielded the characteristic dibasic acid, m.p. 118–119° from acetonitrile, not depressed by an authentic sample.

p-Cymene. Fraction 25 [2 ml., b.p. 70–72° (20 mm.) d_4^{25} 0.8392, n_D^{25} 1.4731, $[\alpha]_D^{25}$ −2.7°] was calculated from the ultraviolet absorption peak at 226 mμ to contain about 17% of myrcene and also showed minor peaks at 264 mμ and 275 mμ which can be attributed to the presence of *p*-cymene. One milliliter of the fraction was shaken with excess thioglycollic acid and later steam-distilled after the addition of excess aqueous alkali, yielding 0.2 ml. of oil. This oil was still contaminated with myrcene (*ca.* 7%) and another unidentified ultraviolet-absorbing constituent (α-phellandrene or α-terpinene?) but showed enhanced peaks at 528 mμ, 264 mμ, and 273 mμ corresponding to the absorption maxima (259 mμ, 265.5 mμ, and 273 mμ) of pure *p*-cymene in 95% alcohol.[14]

Limonene. Of fraction 25, 1.0 ml. was brominated in ether to yield 0.14 g. of crude dipentene tetrabromide of m.p. *ca.* 117° rising after four crystallizations from ethyl acetate to m.p. 122–123° and showing no depression when mixed with authentic dipentene tetrabromide.

Methyl chavicol. Fraction 33 [b.p. 88.3–88.5° (10 mm.) d_4^{25} 0.9592, n_D^{25} 1.5108 $[\alpha]_D^{21.5}$ +1.0°] oxidized with permanganate,[15] gave anisic acid of m.p. and mixture m.p. 182–183° and a lesser quantity of homoanisic acid, m.p. 84–85°. The ultraviolet absorption of fraction 33 in alcohol showed maxima at 226 mμ, 278 mμ, and 284 mμ for which ε was 6650, 1460, and 1180 respectively (*cf.* polyanethole[16] with ϵ_{max} 1500 and 1280 at 278 mμ and 284 mμ respectively). The analytical figures and optical rotation for this fraction reveal the presence of an impurity in the methyl chavicol.

Anal. Calc'd for $C_{10}H_{12}O$: C, 81.04; H, 8.16; OCH_3, 20.9. C, 79.9; 80.0; H, 8.95; 8.79 OCH_3, 13.4.

Unidentified ketone. Fraction 32 [b.p. 87.5–88.3° (10 mm.) d_4^{25} 0.9577, n_D^{25} 1.5055, 1.57 g.] yielded on treatment with Brady's reagent 0.75 g. of crude 2,4-dinitrophenylhydrazone forming dark red crystals, m.p. 210.5–212°, after three crystallizations from ethyl acetate.

Anal. Calc'd for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07; N, 16.86. Found: C, 56.37; H, 5.53; N, 14.28.

The ultraviolet absorption spectrum measured in alcohol showed absorption maxima at 258 mμ and 380 mμ, $E_{1\,cm.}^{1\%}$ being 445 and 853 respectively.

Indian turpentine. Of a sample of *Pinus longifolia* turpentine, (n_D^{25} 1.4735, d_4^{25} 0.8631, $[\alpha]_D^{24}$ +0.9°), 450 ml. were fractionated under 20 mm. pressure in a 6 ft. Podbielniak Heligrid still with a reflux ratio *ca.* 20. The terpenes were collected in 10-ml. fractions and the density and refractive index of each fraction was measured. The fractions, plotted in a *n-d* chart and joined in order, are shown in Fig. III of ref. 5.

α-Thujene. The physical constants of fraction 1 [b.p. 51° (20 mm.), n_D^{25} 1.4623, d_4^{25} 0.8528] indicated a mixture of 4% of α-thujene in α-pinene. Fraction 1 (6.7 g.) oxidized by Delepine's method, yielded 4.9 g. of crude pinonic acid, m.p. 63–65°, and an oily mother liquor which was heated in a stream of carbon dioxide at 260° for one hour. The oily layer (0.1 g.) from the distillate, after washing with sodium bicarbonate solution, was treated with semicarbazide acetate. The crude semicarbazone, m.p. 110–120°, after repeated crystallization from aqueous alcohol, benzene-petroleum ether, and alcohol yielded 5 mg. of thujaketone semicarbazone, m.p. 140–142.5°. This was not depressed in melting point by the addition of an authentic sample of the same melting point prepared from authentic α-thujene[17] from *Eucalyptus dives* oil.

The melting points reported in the literature for this semicarbazone, when prepared from ketone derived from the thujaketonic acids, are 141°,[17,18] 141–142°,[19] 143°,[20] and

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(11) Delepine, *Bull. soc. chim.*, [5] **3**, 1369 (1936).

(12) Naves, *Bull. soc. chim.*, [5] **18**, 990 (1951).

(13) Sutherland and Wilson, *Univ. Queensland Papers, Chem. Dept.*, I, No. 38 (1950).

(14) Owen and Sutherland, unpublished results.

(15) Hasselstrom and Hampton, *J. Am. Chem. Soc.*, **60**, 3086 (1938).

(16) Laitenen, Miller, and Parks, *J. Am. Chem. Soc.*, **69**, 2707 (1947).

(17) Birch and Earl, *Proc. Roy. Soc. New South Wales*, **72**, 55 (1939).

(18) Grütter, Helg, and Schinz, *Helv. Chim. Acta*, **35**, 771 (1952).

(19) Werner and Bogert, *J. Org. Chem.*, **3**, 578 (1939).

(20) Wallach, *Ann.*, **272**, 99 (1893).

145–146°.[21] The lower values result from the difficulty of crystallizing away the semicarbazone of 2,3-dimethylhept-2-en-6-one which Naves[21] has shown is an impurity in crude thujaketone. To avoid this, a further 109 mg. of crude semicarbazone, m.p. 129–134°, was hydrogenated in ethyl acetate using Adams's catalyst and absorbed very nearly the equivalent of one mole of hydrogen. After two crystallizations from ethanol and four from ethyl acetate, the product was obtained as a few milligrams of tabular plates, m.p. 155–156°. The mother liquors yielded 48 mg. of less pure material, m.p. 151–153.5°, $[\alpha]_D$ 0° ± 2° ($CHCl_3$). Similar treatment of crude thujaketone semicarbazone, m.p. 134–136°, from *E. dives* yielded an identical semicarbazone, m.p. 155–156°, not depressed on admixture with that from Indian turpentine.

Anal. Calc'd for $C_{10}H_{21}NO_3$: C, 60.26; H, 10.62; N, 21.08. Found: C, 60.4; H, 10.5; N, 21.6.

This melting point is higher than the values of Naves[21] (151–152°) and Wallach[22] (152–153°) but approximates that (156°,[23] 156–158°)[24] of the optically active semicarbazone ($[\alpha]_D^{18}$ −16.45° in $CHCl_3$).

Myrcene. The physical properties of fraction 8 [n_D^{25} 1.4709, d_4^{25} 0.8465, b.p. 62–65° (20 mm.) $\epsilon_{max.}$ 3280 at 224 mμ in EtOH] indicated a myrcene content[13] of *ca.* 18%. Reaction with maleic anhydride during 0.5 hr. on the water-bath and subsequent hydrolysis gave a 45% yield of the characteristic dicarboxylic acid, m.p. 119°, not depressed by an authentic sample.

(±)-*Limonene.* Of fraction 30 (n_D^{25} 1.4742), d_4^{25} 0.8462, $[\alpha]_D^{26}$ −9.7° one ml. was brominated by Baeyer's method to yield (at −30°) 70 mg. of crude dipentene tetrabromide, m.p. 120–121.5°. Several crystallizations from alcohol gave fine needles, m.p. 122.5–123.5°, not depressed by authentic dipentene tetrabromide.

Terpinolene. Of fraction 32 (n_D^{25} 1.4850, d_4^{25} 0.8554), one ml. was brominated by Bayer's method to yield 1.51 g. of crude terpinolene tetrabromide, m.p. 105–106°, which after two crystallizations from ethyl acetate, melted at 116.5–117°. This depressed the melting point of similarly prepared authentic terpinolene tetrabromide which has been stored at 5° for about a year. Several recrystallizations of the *Pinus longifolia* tetrabromide from ethanol, first lowered the m.p. to 96–97° and then restored it to 116–117°. This material gave a depression (m.p. 97–98°) with the starting material of m.p. 116.5–117°, but no depression with the stored tetrabromide.

The authentic terpinolene tetrabromide was a sample which had been prepared from terpinolene dibromide, m.p. 69–70°, which in turn had been prepared from terpinolene obtained from *Melaleuca linariifolia* oil,[25] the constants of which showed good agreement with literature values for terpinolene.[5,8,26] The unstable and stable tetrabromides have caused confusion previously,[27] and may correspond to the crystal forms A and B described by Henry and Paget[26] who, however, make no reference to mixture melting point tests.

Ozonolysis of fraction 31. A portion (4.2 g.) of this fraction was ozonized in ethyl acetate solution with a 50% calculated excess of ozone. After zinc dust and acetic acid reduction, initially at room temperature and later on the water-bath, 0.38 g. of neutral, steam-volatile oil was separated. From this, after reozonization, less than 10 mg. of neutral, steam-volatile oil was recovered.

Since nopinone, subjected to a similar reozonization may be recovered in 85% yield, the virtual absence of steam-volatile neutral product from the treatment of fraction 31 indicates that appreciable quantities of β-carene were not present.

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(21) Naves and Ardizio, *Bull. soc. chim. France*, 296 (1953).

(22) Wallach, *Ann.*, **381**, 81 (1911).

(23) Guiteras, Nakamiya, and Inhoffen, *Ann.*, **494**, 120 (1932).

(24) Heilbron, Simpson, and Wilkinson *J. Chem. Soc.*, 1699 (1932).

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(26) Henry and Paget, *J. Chem. Soc.*, 29 (1931).

(27) Briasco and Murray, *J. Applied Chem.* (*London*), **2**, 187 (1952).