H_3PO_4 suitable for production of solution fertilizers. For most acids, mole ratio N:P of about 0.175 and weight ratio $CH_3OH:P_2O_5$ of about 3.5 appear to be about optimum for maximum purification with good filtration. A retention time of about 50 min and a minimum temperature of about 50°C are required for good filtration. For most acids these conditions will yield purified acids containing about 1 g of Fe, 0.5 g of Al, and 1.4 g of F/kg of P_2O_5. The removal of Mg depends upon the ratio F:Mg in the raw acid. Up to 90% of the Mg is removed from acids with high ratios of F:Mg, but as little as 20% of Mg is removed from acids with low ratios of F:Mg.

The methanol precipitates contained 46 to 54% P_2O_5 and 4 to 6% nitrogen. All the phosphate was available and about 50% was water soluble by official AOAC procedures. Results from greenhouse tests showed that the precipitates were only slightly less effective than conventional phosphorus sources for corn.

Results from distillation studies showed that the only significant reaction of methanol with phosphoric acid was the formation of momomethylphosphoric acid. Under some conditions dimethyl ether also was formed, but only trace amounts that consume negligible amounts of methanol were formed under normal distillation conditions. Esterification increased with rising temperature and increasing concentration. It was minimized by distillation under vacuum and was virtually eliminated at lower acid concentrations. Distillation of methanol from purified 53% P_2O_5 acid at atmospheric pressure resulted in the esterification of 4.4% of the acid, but in distillation at 0.07 atm only 1.5% of the acid was esterified. These esterification values are equivalent to methanol losses of 40 and 14 lb/ton of P_2O_5, respectively.

Greenhouse tests of technical grade monomethylphosphoric acid as a phosphorus source for corn showed that the ester was equivalent to conventional sources. Thus, small amounts of the ester in the purified acid would be expected to have no adverse agronomic effect.

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Chemistry of Tobacco Constituents. Oxidation of α-Ionone and the Acid-Catalyzed Rearrangement of 5-Keto-α-ionone

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A biosynthetic type synthesis from 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (α-ionone) of some of the cyclic compounds which occur in tobacco and other species has been investigated. Oxidation of α-ionone gave 5-keto-α-ionone, 4-keto-β-ionone, and the tobacco constituent, β-ionone epoxide. In aqueous organic acids, 5-keto-α-ionone cyclizes to 4,4,7-trimethyl-3,4-dihydro-2(1*H*)-naphthalenone, which on reduction and dehydration yielded another natural product of tobacco, 1,2-dihydro-1,1,6-trimethylnaphthalene. Aerial oxidation of 4,4,7-trimethyl-3,4-dihydro-2(1*H*)-naphthalenone gave 4,4,-7-trimethyl-1,4-dihydro-2-hydroxy-1-naphthalenone which has not been described previously.

A number of isoprenoid compounds have been identified in tobacco and its smoke condensate (Stedman, 1968; Tso, 1974). Several of these compounds have been shown to influence the aroma and flavor of tobacco smoke (Demole and Berthet, 1971). Although the biosynthetic origin of cyclic compounds as exemplified by 1,3,7,7-tetramethyl-2-oxabicyclo[4.4.0]dec-5-en-9-one (Figure 1, I) and 1,2-dihydro-1,1,6-trimethylnaphthalene (Figure 1, II) in tobacco (Demole and Berthet, 1972; Kimland et al., 1972) and other plants (Kemp et al., 1971) is uncertain, they may be derived from carotenoids via the intermediate flavor related α-ionone, 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (Figure 1, III) and β-ionone, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (Figure 1, IV) by sequential oxidation, rearrangement, and reduction reactions.

To test the mechanistic feasibility of this proposal, we have reexamined the oxidation of α-ionone and investigated the products formed by protonation and subsequent reduction of the oxidation products in aqueous media. This reaction sequence yielded a cyclic product identical with the natural constituent II found in tobacco (Kimland et al., 1972).

METHODS

Chemicals. α-Ionone was obtained from Dodge and Olcott, Inc., New York, N.Y. All solvents used were of reagent grade.

Spectra. The NMR spectra were run in $CDCl_3$ solutions with a Varian HA-100 spectrometer. Infrared spectra were run on a Perkin-Elmer Model 237 spectrometer. High-resolution mass spectra were obtained on a CEC Model 110 spectrometer at 70 eV.

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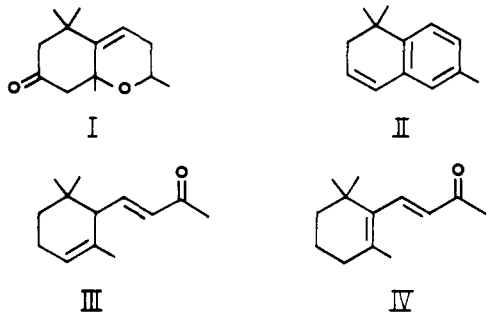

Figure 1. Selected isoprenoid compounds identified in plants.

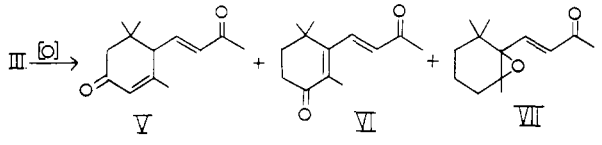

Figure 2. Reaction products of α-ionone with *tert*-butyl chromate.

***tert*-Butyl Chromate Reaction.** α-Ionone was oxidized with *tert*-butyl chromate as described by Prelog and Osgan (1952). The products were separated on a silica gel column by serial elution with Skellysolve F (bp 30–60°C) and ethyl ether. The unreacted α-ionone (10.0% yield) was eluted by Skellysolve–ether (9:1). Sequentially eluted were β-ionone epoxide (Figure 2, VII), 6.0% yield, 4-keto-β-ionone (Figure 2, VI), 14.0% yield, and 5-keto-α-ionone (Figure 2, VI), 21.0% yield, by Skellysolve–ether ratios of 4:1, 7:3, and 1:1, respectively. 4-Keto-β-ionone (mp 52–53°C) was recrystallized from Skellysolve F while 5-keto-α-ionone (mp 72–73°C) was recrystallized from ethyl ether. The melting points were determined on a Kofler hot stage microscope.

The NMR spectrum of 5-keto-α-ionone showed peaks at δ 1.02 (3 H, s) and 1.09 (3 H, s) which indicated the presence of a gem dimethyl group, at δ 1.91 (3 H, s, a vinyl methyl), 2.12 (1 H, d, J = 16.0 Hz), and 2.40 (1 H, d, J = 16.0 Hz) which were ascribed to two geminally coupled methylene protons, at δ 2.29 (3 H, s, an acyl methyl group), 2.73 (1 H, d, J = 9.0 Hz, a methine proton), and 5.98 (1 H, s, a vinyl proton), and two coupled vinyl protons at δ 6.18 (1 H, d, J = 16.0 Hz) and 6.69 (1 H, d of d, J = 9.0, 16.0 Hz). The 5-keto-α-ionone structure was consistent with the infrared and mass spectral data.

Cyclization of 5-Keto-α-ionone. Five grams of the diketone (V) was refluxed under nitrogen for 23 hr in 100 ml of 80% aqueous formic acid. The reaction mixture was cooled for 30 min prior to the addition of 100 ml of water. The mixture was extracted 5 times with ether. This extract was washed 3 times with water and 10% $NaHCO_3$ solution, and 3 additional times with water. The extract was dried over $MgSO_4$ prior to solvent removal under reduced pressure. The product VIII (70% yield) crystallized on cooling. The 2,4-dinitrophenylhydrazone derivatives of VIII and X were prepared according to the method described by Shriner et al. (1956). Compound VIII (400 mg in 100 ml of methanol) was reduced with sodium borohydride (80 mg) to the secondary alcohol IX which was dehydrated to compound II with either aqueous formic acid or *p*-toluenesulfonic acid in benzene. The benzoate of compound IX was prepared by adding 1.0 ml of anhydrous pyridine and 12 drops of benzoyl chloride with vigorous stirring (Shriner et al., 1956). After heating for 5 min on a steam bath, the mixture was cooled and gave, after work-up, the monobenzoate as a colorless oil. Compound VIII was oxidized to X (85% yield) by shaking with an excess of silver oxide in ethanol. The filtered

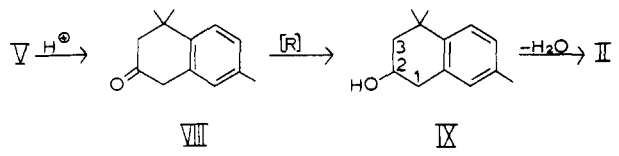

Figure 3. Cyclization of 5-keto-α-ionone and subsequent reduction and dehydration products.

reaction mixture was evaporated and the crystalline residue was recrystallized from ethanol to give X as colorless needles, mp 112–113°C.

RESULTS AND DISCUSSION

Prelog and Osgan (1952) reported that with *tert*-butyl chromate or chromium trioxide, α-ionone yields 5-keto-α-ionone, a compound closely related to a tobacco constituent, 3-oxo-α-ionol (Aasen et al., 1973). In our investigation the *tert*-butyl chromate oxidation products of α-ionone were separated by silica gel chromatography to give V (mp 72–73°C) and two additional products, mp 52–53 and 47–48°C, respectively (Figure 2). The product, mp 52–53°C, showed a band at 1680 cm^{-1} in the infrared spectrum, and its 100-MHz NMR spectrum in $CDCl_3$ showed the presence of a gem dimethyl group (6 H, s, δ 1.21), an allylic methyl group (3 H, d, J = 1.0 Hz, δ 1.81), a methylene group (2 H, t, J = 7.0 Hz, δ 1.90), an acyl methyl ($COCH_3$) (3 H, s, δ 2.37), an acyl methylene ($COCH_2$) group (2 H, t, J = 7.0 Hz, δ 2.55), and two coupled vinylic protons (1 H, d, J = 16.0 Hz, δ 6.19; 1 H, q, J = 16.0, 1.0 Hz, δ 7.25). On the basis of these data and its mass spectrum this product is considered to be identical with 4-keto-β-ionone (VI), a substance previously obtained by *tert*-butyl chromate oxidation of β-ionone (Oppenauer and Oberrauch, 1949). Treatment of VI with aqueous formic acid did not alter the compound. The third oxidation product, mp 47–48°C, of α-ionone has been identified on the basis of its ir, MS, and NMR spectra as β-ionone epoxide (VII). In accord with this structural assignment the NMR spectrum of this product showed the presence of four methyl groups (singlets at δ 0.96, 1.07 (6 H), and 2.30), three methylene groups (4 H, m, δ 1.30–1.60, and 2 H multiplet, δ 1.74–1.97), and two coupled vinylic protons (doublets, J = 16.0 Hz) at δ 6.30 and 7.05. β-Ionone epoxide undergoes acid-catalyzed rearrangements to yield six products, including the tobacco constituent II (Stevens et al., 1976). Warmed with aqueous formic acid in air, 5-keto-α-ionone (V) cyclized to form a low melting product, $C_{13}H_{16}O$ (Figure 3, VIII), in high yield (70%) together with small amounts of an oxidation product, $C_{13}H_{14}O_2$. The ir spectrum of the $C_{13}H_{16}O$ product has a major band at 1728 cm^{-1} indicative of an unconjugated carbonyl, yields a crystalline mono(2,4-dinitrophenylhydrazone) derivative, mp 173–174°C, and has now been identified as 4,4,7-trimethyl-3,4-dihydro-2(1*H*)-naphthalenone (VIII). In accordance with this structural assignment the NMR spectrum showed a gem dimethyl group (6 H, s, δ 1.33), an aromatic methyl group (3 H, s, δ 2.34), a methylene group (2 H, s, δ 2.53), a benzylic methylene group adjacent to carbonyl (2 H, s, δ 3.64), and three aromatic protons at δ 6.94, 7.07, and 7.32 with couplings characteristic of a 1,2,4 substitution pattern. High-resolution mass spectral analysis confirmed the molecular formula as $C_{13}H_{16}O$ while low resolution gave m/e 145 (100), 173 (80), 188 (52), 146 (24), 131 (13), 128 (13), 129 (12), 115 (12), 105 (12), 174 (11), and 130 (11). Structure VIII was further confirmed by reduction of the cyclization product with sodium borohydride to give the secondary alcohol IX (Figure 3), in which the axial methine proton at C_2 appears as a 16-line multiplet (J = 4.0, 5.5,

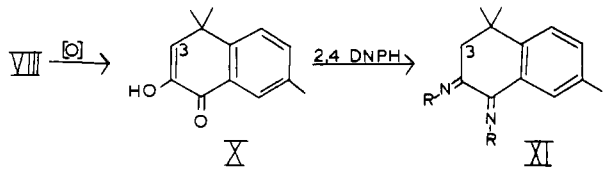

Figure 4. Oxidation product of 4,4,7-trimethyl-3,4-dihydro-2(1*H*)-naphthalenone and its 2,4-dinitrophenylhydrazone derivative.

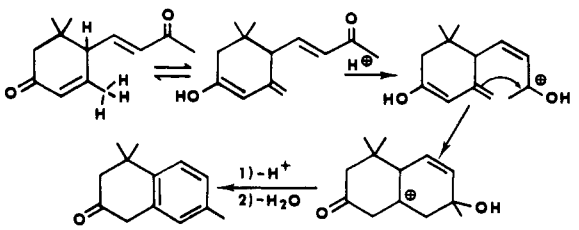

Figure 5. A suggested mechanism from 5-keto-α-ionone to 4,4,7-trimethyl-3,4-dihydro-2(1*H*)-naphthalenone.

11.0, 11.0 Hz) at δ 4.15, the axial proton at C_3 as a double doublet (J = 11.0, 12.5 Hz) at δ 1.65, the equatorial proton resonates as a double quartet (J = 2.0, 4.0, 12.5 Hz) at δ 1.94, the axial benzylic proton at C_1 as a double doublet (J = 11.0, 16.0 Hz) at δ 2.68, and the equatorial benzylic proton at C_1 as a double quartet (J = 2.0, 5.5, 16.0 Hz) at δ 3.08. As expected the benzoate (oil) of IX showed a downfield shift of the C_2 methine proton from δ 4.15 to 5.49. Dehydration of the secondary alcohol IX with warm aqueous formic acid, or better, with *p*-toluenesulfonic acid in benzene, gave the natural hydrocarbon II (Figure 3). The infrared spectrum of this compound corresponded to that published by Kemp et al. (1971) and to a spectrum obtained in our previous research (Stevens et al., 1976). The GLC retention time on a Igepal column (75 ft × 0.01 in.) was identical with that previously obtained. Although VIII does not appear to have been previously described, a compound with this structure was mentioned briefly without further description or detail as a minor by-product in a patented synthesis of 1-hydroxy-4-keto-α-ionone (Rowland, 1971).

When exposed to air or, better, treated with silver oxide, VIII is converted into the new product, $C_{13}H_{14}O_2$, mp 112–113°C (Figure 4, X). This product, λ_{max} (ε) 298 (9400) and 258 (11000) nm in ethanol, shows strong absorption bands in the infrared at 3430 (hydroxyl) and 1655 cm^{-1} (conjugated carbonyl). On the basis of its NMR spectrum, it is considered to be 4,4,7-trimethyl-1,4-dihydro-2-hydroxy-1-naphthalenone, i.e., the vinylic proton at C_3 appears as a sharp singlet at δ 6.21 and the hydroxyl as a broad 1 H peak at δ 6.46. High-resolution mass spectral analysis confirmed the molecular formula as $C_{13}H_{14}O_2$, while low resolution gave m/e 39 (100), 91 (92), 115 (89), 51 (82), 159 (77), 77 (60), 43 (58), 65 (54), 63 (53), and 27 (48). In further confirmation of this structural assignment, X reacts in its diketonic form with 2,4-dinitrophenylhydrazone to give a crystalline bis(2,4-dinitrophenylhydrazone) derivative (mp 255–257°C) of structure XI (Figure 4) (R = 2,4-$(NO_2)_2C_6H_3NH$–). In XI, the methylene protons at C_3 appear, as expected, as a 2 H singlet at δ 2.87.

The acid-catalyzed cyclization of 5-keto-α-ionone may be rationalized as shown in Figure 5.

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Identification of Salsolinol as a Major Dopamine Metabolite in the Banana

Ralph M. Riggin, Michael J. McCarthy, and Peter T. Kissinger*

A major pathway of dopamine metabolism in the banana involves reaction with endogenous acetaldehyde and condensation to form 1-methyl-6,7-dihydroxy-1,2,3,4-tetrahydroisoquinoline. The process accelerates during advanced stages of ripening due to the increased production of acetaldehyde. The new metabolite was found using a combination of liquid chromatography and thin-layer electrochemistry. Structural confirmation was obtained by cyclic voltammetry, thin-layer chromatography, and gas chromatography–mass spectrometry.

During the course of an investigation of tyrosine metabolism in the banana using liquid chromatography with electrochemical detection (LCEC), an unidentified phenol appeared in high concentration during later stages of ripening. This species, 1-methyl-6,7-dihydroxy-1,2,3,4-tetrahydroisoquinoline (salsolinol), has apparently not been previously reported in plant matter.

A new technique (LCEC) has been under development

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