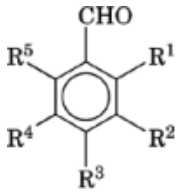
Kirk-Othmer Encyclopedia of Chemical Technology.

HYDROXYBENZALDEHYDES

Hydroxybenzaldehydes are organic compounds of the general formula:



where R^1 through $R^5 = H$ or OH but at least one R group is OH. All of the isomeric mono-, di-, and trihydroxybenzaldehydes have been isolated (Table 1). The higher polyhydroxybenzaldehydes are unknown (12). This article deals primarily with *p*-hydroxybenzaldehyde [123-08-0] and salicylaldehyde [90-02-8] which together represent more than 99% of the hydroxybenzaldehydes market.

Of the two commercially important monohydroxybenzaldehydes the ortho isomer (salicylaldehyde) is the more important one. Salicylaldehyde (salicylic aldehyde, salicylal) is a colorless, oily liquid, the only hydroxybenzaldehyde liquid at room temperature with a pungent irritating odor. It occurs naturally in beer, oils of spirea, bird cherries and cassia, and in coffee, grape, tea, and tomato (13, 14). (see Benzaldehyde). Salicylaldehyde and its derivatives are utilized as ingredients in agricultural chemicals, electroplating, perfumes, petroleum chemicals, polymers, and Fibers (qv).

p-Hydroxybenzaldehyde (4-formylphenol) is a colorless to faint tan solid, with a slight, agreeable, aromatic odor. It occurs naturally in some plants in small amounts (15–17).

1. Physical Properties

Physical constants for salicylaldehyde and *p*-hydroxybenzaldehyde are listed in Table 2. Spectral data have been published (Table 2).

The location of the hydroxyl and aldehyde groups ortho to one another in salicylaldehyde permits intramolecular hydrogen bonding, and this results in the lower melting point and boiling point and the higher acid dissociation constant observed relative to *p*-hydroxybenzaldehyde.

2. Chemical Properties

The effect of the aldehyde group on the phenolic hydroxyl group is primarily an increase in its acidity: both 2-hydroxy- and 4-hydroxy*benzaldehydes* are stronger acids than phenol (pK_a (H_2O, 20°C) = 9.89; see Table 2 for comparison). The aldehyde group, however, has little effect on the reaction of the hydroxyl group.

Table 1. Physical Properties of Hydroxybenzaldehydes

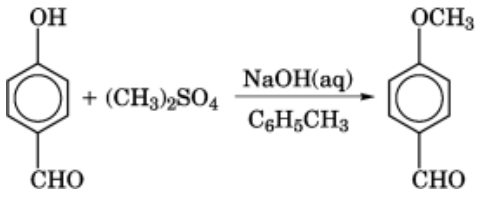
Chemical Abstracts name	Mol wt	CAS Registry Number	Common name	Mp, °C	Reference	Bp, °C[a]
2-hydroxybenzaldehyde	122.12	[90-02-8]	salicylaldehyde	−7	1	197
3-hydroxybenzaldehyde	122.12	[100-83-4]	*m*-hydroxybenzaldehyde	108	1	240
4-hydroxybenzaldehyde	122.12	[123-08-0]	*p*-hydroxybenzaldehyde	117	1,2	310
2,3-dihydroxybenzaldehyde	138.12	[24677-78-9]	*o*-pyrocatechualdehyde	105–107	3	
2,4-dihydroxybenzaldehyde	138.12	[95-01-2]	*β*-resorcylaldehyde	201–202	1	220–228[b]
2,5-dihydroxybenzaldehyde	138.12	[1194-98-5]	gentisaldehyde	97–98	4	99[c]
2,6-dihydroxybenzaldehyde	138.12	[387-46-2]	*γ*-resorcylaldehyde	154–155	5	
3,4-dihydroxybenzaldehyde	138.12	[139-85-5]	protocatechualdehyde	154 (dec)	1	
3,5-dihydroxybenzaldehyde	138.12	[26153-38-8]	*α*-resorcylaldehyde	161–162	6	
2,3,4-trihydroxybenzaldehyde	154.12	[2144-08-3]		179–180	7	
2,3,5-trihydroxybenzaldehyde	154.12	[74186-01-9]		187	8	
2,3,6-trihydroxybenzaldehyde	154.12	[64168-39-4]		170–180 (dec)	9	
2,4,5-trihydroxybenzaldehyde	154.12	[35094-87-2]		223	10	
2,4,6-trihydroxybenzaldehyde	154.12	[487-70-7]	phloroglucinaldehyde	292–295 (dec)	7	
3,4,5-trihydroxybenzaldehyde	154.12	[13677-79-7]	gallaldehyde	210	11	

[a]At 100 kPa = 0.987 atm unless otherwise noted.
[b]At 2.9 kPa[d]
[c]At 1.6 kPa[d].
[d]To convert kPa to mm Hg, multiply by 7.5.

The deactivating effect of the phenolic hydroxyl on the aldehyde group is more pronounced, but the hydroxybenzaldehydes still undergo most of the normal aldehyde reactions.

2.0.1. Reactions of the Hydroxyl Group

The hydroxyl proton of hydroxybenzaldehydes is acidic and reacts with alkalies to form salts. The lithium, sodium, potassium, and copper salts of salicylaldehyde exist as chelates. The cobalt salt is the most simple oxygen-carrying synthetic chelate compound (33). The stability constants of numerous salicylaldehyde–metal ion coordination compounds have been measured (34). Both salicylaldehyde and 4-hydroxybenzaldehyde are readily converted to the corresponding anisaldehyde by reaction with a methyl halide, methyl sulfate (35–37), or methyl carbonate (38). The reaction shown produces *p*-anisaldehyde [123-11-5] in 93.3% yield. Other ethers can also be made by the use of the appropriate reagent.



2.0.2. Reactions of the Aromatic Ring

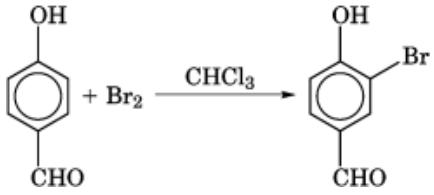
The aromatic ring of hydroxybenzaldehydes participates in several typical aromatic electrophilic reactions.

2.0.2.1. Halogenation. Chlorination and bromination yield mono- and dihalo derivatives, depending on reaction conditions. Bromination of *p*-hydroxy-benzaldehyde in chloroform yields 65–75% of the product shown (39).

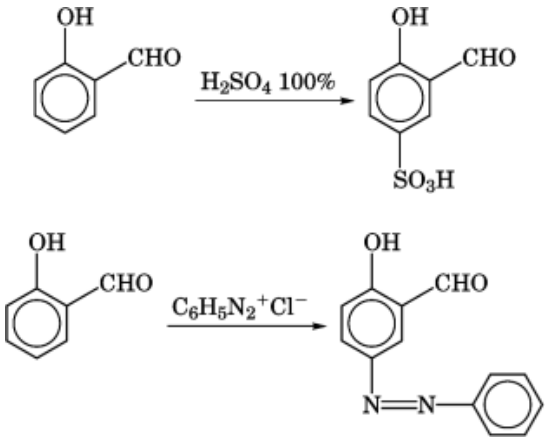
Table 2. Physical and Spectral Data for o- and p-Hydroxybenzaldehydes

	Salicylaldehyde		*p*-Hydroxybenzaldehyde	
Property	Value	Reference	Value	Reference
		Physical data		
bp, °C (kPa)[a]	93 (3.3)	18	170 (1.3)	23
	80 (1.6)	19		
vapor pressure		20		28
density, g/cm^3	1.167 (20°C)	21	1.143 (117°C)	29
solubility, g/100 g water	1.7 (86°C)	22	1.3 (30.5°C)	22
acid dissociation constant pK_a, H_2O, 25°C	8.14	23	7.6	23
		Spectral data		
infrared		24		30
ultraviolet		25		25
proton nmr		26		31
mass spectra		27		32

[a]To convert kPa to mm Hg, multiply by 7.5.



2.0.2.2. Sulfonation and Diazonium Coupling. Like phenol, salicylaldehyde reacts easily in these reactions (40, 41), with a high para-selectivity.



2.0.3. Reactions of the Aldehyde Group

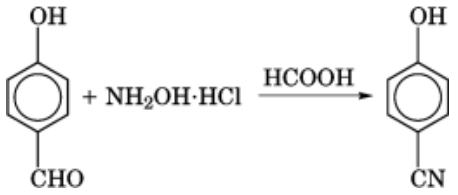
2.0.3.1. Oxidation. Oxidation of hydroxybenzaldehydes can result in the formation of a variety of compounds, depending on the reagents and conditions used. Replacement of the aldehyde function by a hydroxyl group results when 2- or 4-hydroxybenzaldehydes are treated with hydrogen peroxide in acidic (42) or basic (43) media: pyrocatechol or hydroquinone are obtained, respectively.

Salicylaldehyde is readily oxidized, however, to salicylic acid by reaction with solutions of potassium permanganate, or aqueous silver oxide suspension. 4-Hydroxybenzaldehyde can be oxidized to 4-hydroxybenzoic acid with aqueous silver nitrate (44). Organic peracids, in basic organic solvents, can also be used for these transformations into benzoic acids (45). Another type of oxidation is the reaction of salicylaldehyde with alkaline potassium persulfate, which yields 2,5-dihydroxybenzaldehyde (46).

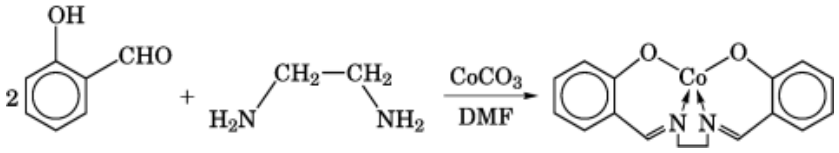
2.0.3.2. Canizzaro Reaction. Both 2- and 4-hydroxybenzaldehydes undergo this self-oxidation–reduction reaction, but much less readily than benzaldehyde; the reaction requires metal catalysts such as nickel, cobalt, or silver to yield the corresponding hydroxybenzoic acids and hydroxybenzyl alcohols (47, 48).

2.0.3.3. Reduction. These hydroxybenzaldehydes can be reduced by catalytic hydrogenation over palladium or platinium to yield the corresponding hydroxybenzyl alcohols, but the electrolytic reduction in an alkaline medium gives the coupling product 1,2-bis(4-hydroxyphenyl)ethane-1,2-diol in very good yield from 4-hydroxybenzaldehyde (49–51).

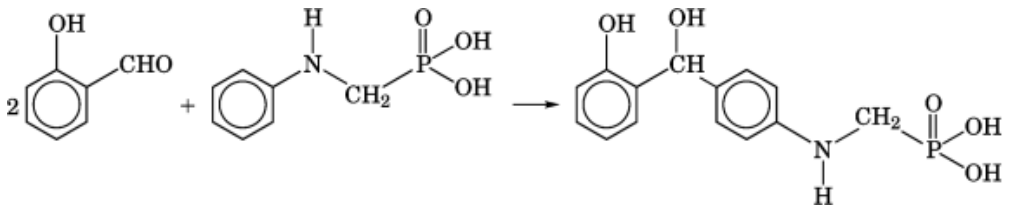
2.0.3.4. Reactions with Amines and Amides. Hydroxybenzaldehydes undergo the normal reactions with aliphatic and aromatic primary amines to form imines and Schiff bases; reaction with hydroxylamine gives an oxime, reaction with hydrazines gives hydrazones, and reactions with semicarbazide give semicarbazones. The reaction of 4-hydroxybenzaldehyde with hydroxylamine hydrochloride is a convenient method for the preparation of 4-cyanophenol (52, 53).



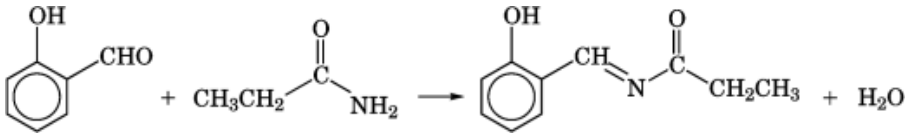
Many excellent chelating agents are prepared by the reaction of salicylaldehyde with 1,2- or 1,3-diaminoalkanes and have wide use in chemistry, for example as oxidation catalysts (see Chelating agents) (54–56).



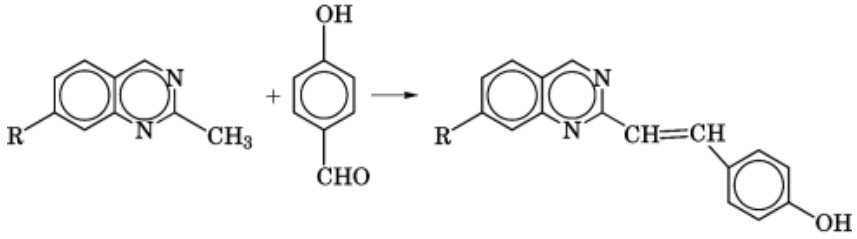
The reaction product of salicylaldehyde and a secondary aniline is the benzylic alcohol, with total para-selectivity (57). The yield is 93%.



Primary amides condense with hydroxybenzaldehydes in a manner similar to amines. This reaction is often conducted in the presence of sodium acetate or an organic base such as pyridine. For example, the reaction of salicylaldehyde and propionamide produces salicylidene propionamide (58).

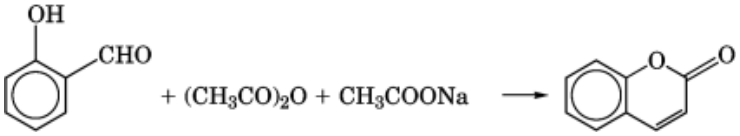


Hydroxybenzaldehydes readily react with compounds containing methyl or methylene groups bonded to one or two carboxyl, carbonyl, nitro, or similar strong electron-withdrawing groups. The products are usually β-substituted styrenes. 4-Hydroxybenzaldehyde, for example, reacts with 2-methylquinazolines (where R = H, Cl) to give compounds which have anti-inflammatory activity (59).



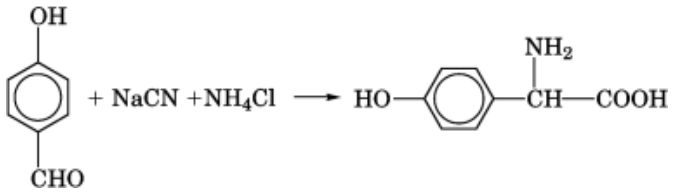
2.0.3.5. Aldol Reactions. In the same way, hydroxybenzaldehydes react readily with aldehydes and ketones to form α,β-unsaturated carbonyl compounds in the Claisen-Schmidt or crossed-aldol condensation (60).

2.0.3.6. Perkin Reaction. A product of significant commercial importance, coumarin [91-64-5], is made by the reaction of salicylaldehyde with acetic anhydride and sodium acetate, a Perkin reaction (61).



2.0.4. Other Reactions

The reaction of 4-hydroxybenzaldehyde with sodium cyanide and ammonium chloride, Strecker synthesis, yields *p*-hydroxyphenylglycine [938-97-6], a key intermediate in the manufacture of semisynthetic penicillins and cephalosporins (see Antibiotics, β-lactams).



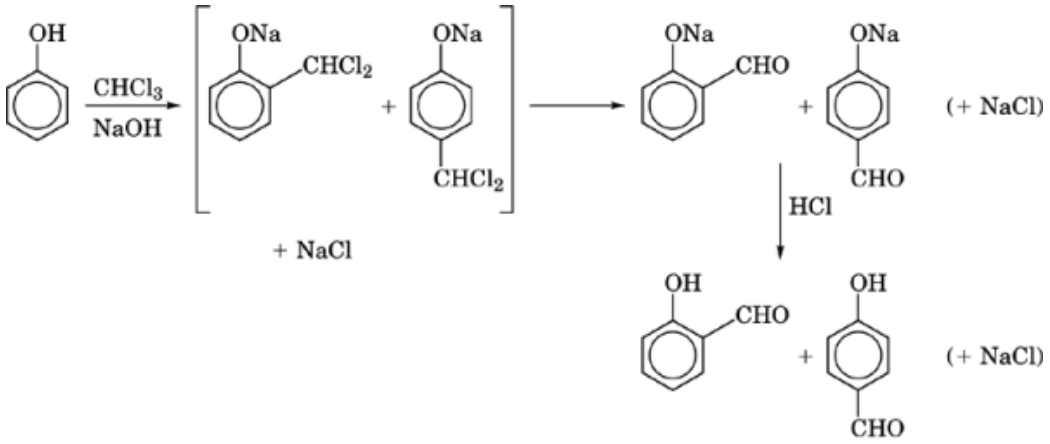
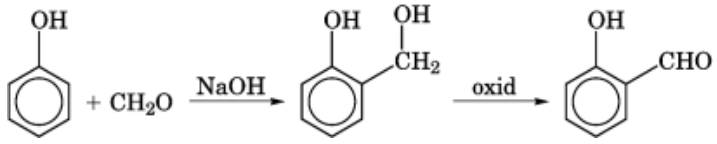


Fig. 1. Production of hydroxybenzaldehydes by the Reimer-Tiemann process.

3. Manufacture

The main processes for the manufacture of hydroxybenzaldehydes are based on phenol. The most widely used process is the saligenin process. Saligenin (2-hydroxybenzyl alcohol [90-01-7]) and 4-hydroxybenzyl alcohol [623-05-2] are produced from base-catalyzed reaction of formaldehyde with phenol (35). Air oxidation of saligenin over a suitable catalyst such as platinium or palladium produces salicylaldehyde (62).



Reaction of phenyl metaborate with formaldehyde, followed by catalytic oxidation, has been reported to give salicylaldehyde selectively and directly from phenol without isolation of any intermediate products (63).

Although 4-hydroxybenzaldehyde can be made by the saligenin route, it has been made historically by the Reimer-Tiemann process, which also produces salicylaldehyde (64). Treatment of phenol with chloroform and aqueous sodium hydroxide results in the formation of benzal chlorides, which are rapidly hydrolyzed by the alkaline medium into aldehydes. Acidification of the phenoxides results in the formation of the final products, salicylaldehyde and 4-hydroxybenzaldehyde. The ratio of ortho and para isomers is flexible and can be controlled within certain limits. The overall reaction scheme is shown in Figure 1. Product separation is accomplished by distillation, but this process leads to environmental problems because of the quantities of sodium chloride produced.

Other routes for hydroxybenzaldehydes are the electrolytic or catalytic reduction of hydroxybenzoic acids (65, 66) and the electrolytic or catalytic oxidation of cresols (67, 68). (see Salicylic acid and related compounds). Salicylaldehyde is available in drums and bulk quantities. The normal specification is a freezing point minimum of 1.4°C. 4-Hydroxybenzaldehyde is available in fiber drums, and has a normal specification requirement of a 114°C initial melting point. More refined analytical methods are used where the application requires more stringent specifications.

4. Economic Aspects

Rhône-Poulenc (RP), producing both in Europe and the United States, is the only producer of salicylaldehyde worldwide, for merchant sales. A large portion of it is used captively in the manufacture of coumarin. The remainder is available for the merchant market.

Worldwide capacity figures for salicylaldehyde are not published; however, the estimated capacity is approximately $4000 - 6000$ t/y. The supply–demand picture for salicylaldehyde has been well balanced in the 1990s, as RP has expanded capacity to meet the growing market need. The price of salicylaldehyde was fairly stable at approximately \$2.20/kg during the late 1970s and early 1980s; however, prices rose rapidly in the mid-1970s. The 1980 price of salicylaldehyde was in the \$6.00/kg range; the 1994 price is now stable in the same range.

Chuo Kasein (Japan), various Chinese companies, and Hoechst (France) are producers of *p*-hydroxybenzaldehyde.

5. Health and Safety Factors

Salicylaldehyde has a moderate acute oral toxicity; the LD_{50} for rats is $0.3 - 2.0$ g/kg of body weight. *p*-Hydroxybenzaldehyde has a low acute oral toxicity; the LD_{50} for rats is 4.0 g/kg of body weight. Neither material is likely to present a problem from ingestion incidental to its handling and industrial use. It should be recognized, however, that serious effects may result if substantial amounts are swallowed.

Tests performed on rabbits indicate that neither material is absorbed through the skin in toxic amounts. Skin contact with *p*-hydroxybenzaldehyde is essentially nonirritating; however, contact with salicylaldehyde is capable of causing a severe burn, especially in case of prolonged or repeated contact. Hence, such contact should be avoided. *p*-Hydroxybenzaldehyde is slightly irritating to the eyes and can cause slight transient irritation and slight transient corneal injury. Salicylaldehyde is appreciably irritating to the eyes and may cause pain, irritation, and some corneal injury.

6. Uses

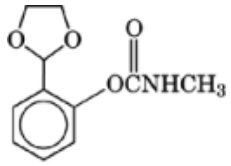
The hydroxybenzaldehydes are used primarily as chemical intermediates for a variety of products. The largest single use of salicylaldehyde is in the manufacture of coumarin. Coumarin is an important commercial chemical used in soaps, flavors and fragrances, and electroplating (see Coumarin). Other significant uses of both salicylaldehyde and *p*-hydroxybenzaldehyde are as follows.

6.0.5. Agricultural Chemicals

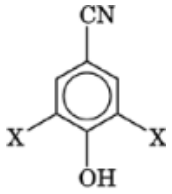
Salicylaldehyde is a valuable intermediate in the manufacture of Herbicides (qv) and pesticides. The phenylhydrazones of salicylaldehyde are used to inhibit cereal rusts (69), and as herbicides for a variety of weed species (70), eg, *Amaranthus retroflexus*. In addition, both the hydrazone and phenylhydrazone of salicylaldehyde have been found to be effective antimicrobials (71) (see Disinfectants; Iindustrial antimicrobial agents). The *N*-methyl- and *N,N*-dimethylcarbamates of salicylaldehyde acetals and mercaptals are effective insecticides; the *N*-methylcarbamate of the cyclic acetal of salicylaldehyde (from salicylaldehyde and ethylene glycol) is an important commercial insecticide(72). This product, dioxacarb [6988-21-2], [2-(1,3-dioxolan-2-yl)phenyl-*N*-methylcarbamate] **(1)**, is widely used in European and African countries for the protection of potatoes and cocoa (73) (see Insect control technology). Another important use of salicylaldehyde is in the synthesis of

micronutrients. In particular, ferric ion chelates have been used on alkaline or calcerous soils which can occur in citrus or olive groves (see Fertilizers; Mineral nutrients).

p-Hydroxybenzaldehyde has extensive use as an intermediate in the synthesis of a variety of agricultural chemicals. Halogenation of *p*-hydroxybenzaldehyde, followed by conversion to the oxime, and subsequent dehydration results in the formation of 3,5-dihalo-4-hydroxybenzonitrile **(2)**. Both the dibromo- and diiodo-compounds are commercially important contact herbicides, bromoxynil [1689-84-5] (**2**) where X = Br, and ioxynil [1689-83-4](**2**), where X = I respectively (74). Several hydrazone derivatives have also been shown to be active herbicides (70).



(**1**)



(**2**)

6.0.6. Electroplating

Salicylaldehyde is a starting material in the synthesis of Coumarin (qv) which is widely used by the Electroplating (qv) industry as a brightener and leveling agent in nickel plating. The imine resulting from the reaction of salicylaldehyde with an alkanolamine (containing a primary amine group) is an effective brightening agent in the electroplating of zinc on iron and steel (75). In another zinc Electroplating (qv) process in a noncyanide alkaline bath containing a polyaminesulfone, salicylaldehyde itself was found to aid in producing a bright zinc electroplate on steel (76).

Both *p*-hydroxybenzaldehyde and its methyl ether, *p*-methoxybenzaldehyde [123-11-5] (*p*-anisaldehyde) have found extensive use in electroplating. The most widespread application has been in alkaline bright zinc plating, both in non-cyanide (77) and in cyanide-containing (78) baths. The aldehydes act as both brightening and leveling agents.

6.0.7. Flavors and Fragrances

Salicylaldehyde is a starting material in the synthesis of coumarin, which finds extensive use in the Soap (qv) and Perfume (qv) industries and salicylaldehyde can be used itself as a preservative in essential oils and perfumes (see Oils, essential). The antibacterial activity of salicylaldehyde is strong enough to allow its use at very low concentrations (79).

p-Hydroxybenzaldehyde has an agreeable aromatic odor, but is not itself a fragrance. It is, however, a useful intermediate in the synthesis of fragrances. The methyl ether of *p*-hydroxybenzaldehyde, ie, *p*-anisaldehyde, is a commercially important fragrance. *p*-Anisaldehyde can be made in a simple one-step synthesis from *p*-hydroxybenzaldehyde and methyl chloride. Another important fragrance, 4-(*p*-hydroxyphenyl)butanone,

commonly referred to as raspberry ketone, can be prepared from the reaction of *p*-hydroxybenzaldehyde and acetone, followed by reduction (see Flavors and spices).

6.0.8. Petroleum Products

Condensation products of salicylaldehyde and amines are used in various forms for the removal or neutralization of the metallic ions that cause oxidative degradation in petroleum products. The product formed from propylenediamine and salicylaldehyde, ie, *N,N′*-disalicylidene-1,2-propanediamine, has proven itself to be a commercially important chelating agent, primarily because of its combination of outstanding chelation properties plus its solubility in oil (80). Other adducts are used as detergents in lubricating oils and gasoline (81), as sludge inhibitors in fuel oils and gasoline (82) and as antioxidants to improve the high temperature stability of polyester lubricants (83), gasoline (84), and petroleum oils (85).

6.0.9. Pharmaceuticals

p-Hydroxybenzaldehyde is often a convenient intermediate in the manufacture of Pharmaceuticals (qv). For example, 2-(*p*-hydroxyphenyl)glycine can be prepared in a two-step synthesis starting with *p*-hydroxybenzaldehyde (86). This amino acid is an important commercial intermediate in the preparation of the semisynthetic penicillin, amoxicillin (see Antibiotics, β-lactams). Many cephalosporin-type antibiotics can be made by this route as well (87). The antiemetic trimethobenzamide [138-56-7] is conveniently prepared from *p*-hydroxybenzaldehyde (88) (see Gastrointestinal agents).

6.0.10. Polymer Applications

The reaction of salicylaldehyde with poly(vinyl alcohol) to form an acetal has been used to provide dye receptor sites on poly(vinyl alcohol) fibers (89) and to improve the light stability of blend fibers from vinyl chloride resin and poly(vinyl alcohol) (90) (see Fibers, poly(vinyl alcohol)).

The metal coordination complexes of both salicylaldehyde phenylhydrazone (91) and salicylaldoxime provide antioxidant (92) protection and uv stability to polyolefins (see Antioxidants). In addition, the imines resulting from the reaction of salicylaldehyde and aromatic amines, eg, *p*-aminophenol or α-naphthylamine, can be used at very low levels as Heat stabilizers (qv) in polyolefins (93).

The resiliency and dyeability of poly(vinyl alcohol) fibers is improved by a process incorporating *p*-hydroxybenzaldehyde to provide a site for the formation of a stable Mannich base. Hydroxyl groups on the fiber are converted to acetal groups by *p*-hydroxybenzaldehyde. Subsequent reaction with formaldehyde and ammonia or an alkylamine is rapid and forms a stable Mannich base that is attached to the polymer backbone (94).

6.0.11. Miscellaneous

The reaction products of salicylaldehyde with certain compounds containing active methylene groups, eg, acetylacetone, are excellent uv absorbers. Films containing these compounds can be used as uv filters to protect light-sensitive foods, wood products, paper, dyes, fibers, and plastics (95).

The reaction product of salicylaldehyde and hydroxylamine, salicylaldoxime, has been found to be effective in photography in the prevention of fogging of silver halide emulsions on copper supports (96). It also forms the basis for an electrolytic facsimile-recording paper (97) and in combination with a cationic polymer, is used in another electrolytic dry-recording process (98) (see Electrophotography).

The copper-chelating ability of salicylaldoxime has been used to remove copper from brine in a seawater desalination plant effluent. A carbon–sorbate bed produced by sorption of the oxime on carbon proved to be extremely effective in the continuous process (99). In another application, the chelating ability of salicylaldoxime with iron and copper was used to stabilize bleaching powders containing inorganic peroxide salts (100).

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