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SALTS OF L-ASCORBIC ACID WITH CERTAIN SUBSTITUTED AMINES AND TRIPHENYLPHOSPHINE

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L-Ascorbic acid (2,3-dehydro-L-gulonic acid γ-lactone, vitamin C, **1a**) plays an important role in metabolism [1, 2]. It is a strong reductant owing to the presence of an endiol C(OH)=C(OH). It participates in regulation of redox processes, carbon exchange, blood turnover, tissue regeneration, and formation of steroidal hormones. One of the important physiological functions of **1a** is the involvement in procollagen and collagen synthesis and normalization of capillary perfusion. L-Ascorbic acid and its salts, sodium, magnesium, calcium ascorbates, are used as medicinal preparations [1]. The acidic properties of **1a** ($pK_1 = 4.17$, $pK_2 = 11.57$) are due to the 3-OH and partially the 2-OH [2, 3]. The γ-lactone of **1a** is not hydrolyzed by weak bases [2].

Functionally substituted N- and P-containing salts of natural carboxylic acids (resinous, bile, nicotinic, maleopimaric) are interesting because of their wide spectrum of biological activities [4-7]. The L-ascorbates of certain amines (derivatives of functionally substituted guanidines and benzylamines) also have bactericidal, antiatherosclerotic, and hypolipidemic activity [8-10].

Our goal was to develop a preparative method for synthesizing new biologically active L-ascorbates of certain functionally substituted amines and triphenylphosphine. The optimal conditions for synthesizing previously known salts **1b-ac** are the reaction of **1a** with the corresponding aliphatic, aromatic, and heterocyclic amines and triphenylphosphine in stoichiometric ratios (1:1) in absolute CH_3OH. The reactions were complete after 5-10 min at 30-40°C. Yields of **1b-ac** were 92-96% after removal of CH_3OH in vacuum and heating for 4-5 h at 30-40°C.

The resulting salts had the following melting points and compositions: **1b**, 51°C, $C_{22}H_{43}NO_6$; **1c**, 55°C, $C_{24}H_{47}NO_6$; **1d**, 85°C, $C_{12}H_{14}BrNO_6$; **1e**, 42°C, $C_{18}H_{19}NO_6$; **1f**, 68°C, $C_{20}H_{23}NO_6$; **1g**, 84°C, $C_{27}H_{29}NO_6$, **1h**, 132°C, $C_{12}H_{15}NO_7$; **1i**, 65°C, $C_{15}H_{19}NO_7$; **1j**, 34°C, $C_{17}H_{23}NO_7$, **1k**, 132°C, $C_{15}H_{19}NO_7$; **1l**, 157°C, $C_{13}H_{15}NO_8$; **1m**, 82°C, $C_{15}H_{19}NO_8$; **1n**, 48°C, $C_{17}H_{23}NO_8$; **1o**, 144°C $C_{18}H_{19}NO_6$; **1p**, 162°C, $C_{16}H_{17}NO_6$; **1q**, 103°C, $C_{16}H_{17}NO_6$; **1r**, 161°C, $C_{24}H_{21}NO_6$; **1s**, 65°C, $C_{16}H_{25}NO_7$; **1t**, 73°C, $C_{15}H_{15}NO_7$; **1u**, 48°C, $C_{12}H_{16}N_2O_6$; **1v**, 71°C, $C_{12}H_{16}N_2O_6$; **1w**, 165°C, $C_{23}H_{28}N_2O_7$; **1x**, 108°C, $C_{20}H_{23}N_3O_6$; **1y**, 48°C, $C_{12}H_{16}N_2O_6$; **1z**, 192°C, $C_{20}H_{17}NO_8$; **1aa**, 224°C, $C_{19}H_{18}N_2O_6$; **1ab**, 92°C, $C_{12}H_{13}N_3O_6$; **1ac**, 72°C, $C_{24}H_{23}PO_6$.

Salts **1b-ac** are colorless or colored friable crystalline compounds that are very soluble in methanol and ethanol, slightly soluble in acetone and water, and insoluble in hexane, benzene, and chloroform. They are not hygroscopic and store well in the dark in sealed ampuls at 0-5°C. The structures of the synthesized salts **1b-ac** were confirmed by elemental analyses, IR spectra, and PMR spectra. The IR spectra of **1b-ac** contain absorption bands for OH at 3500-3000 cm^{-1}; C=O, 1720-1750; C=C, 1585-1680; C–O, 1310-1370, 1110-1130, and 1120-1130. The purities of the products were 98 ± 1%.

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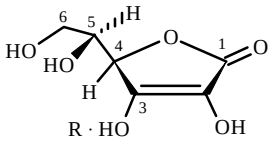

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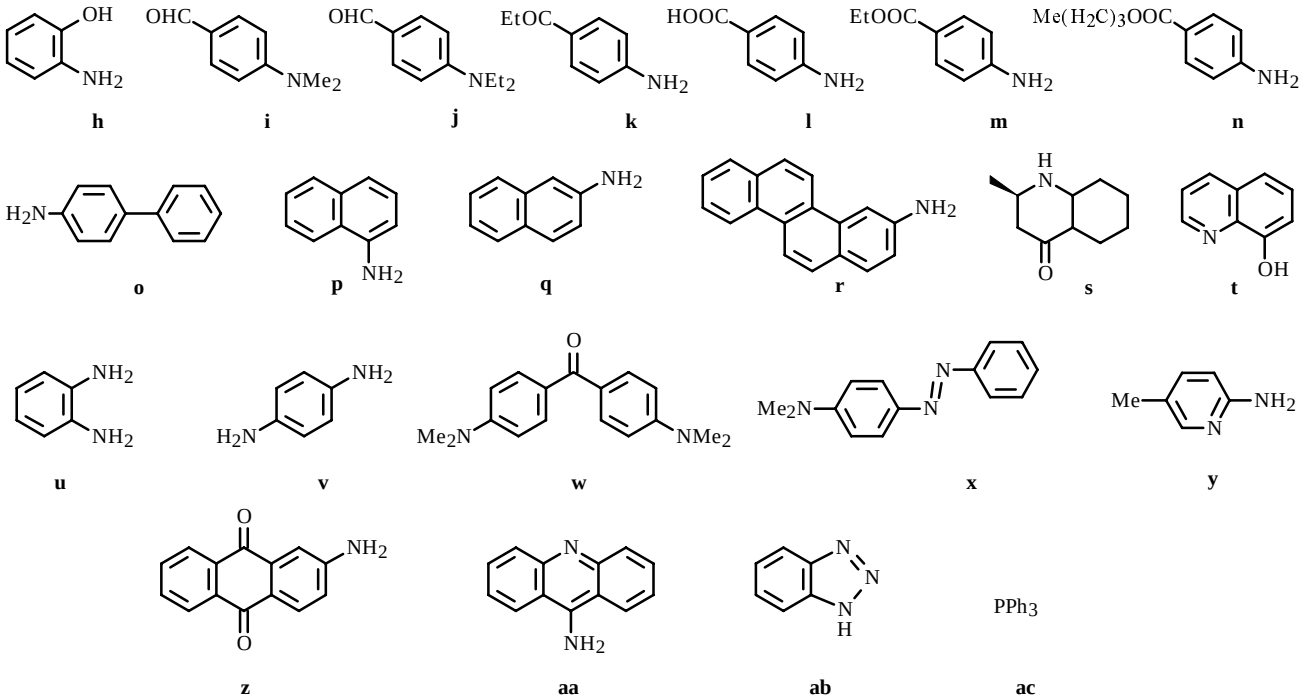
R missing **a** | $Me(CH_2)_{15}NH_2$ **b** | $Me(CH_2)_{17}NH_2$ **c** | $4\text{-}BrC_6H_4NH_2$ **d** | Ph_2NH **e** | $(4\text{-}MeC_6H_4)_2NH$ **f** | $(PhCH_2)_3N$ **g**



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