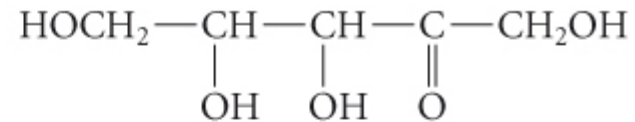
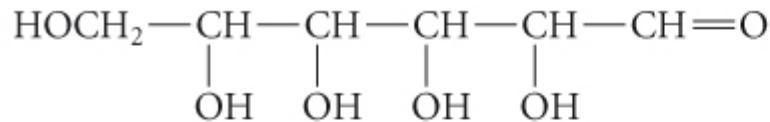
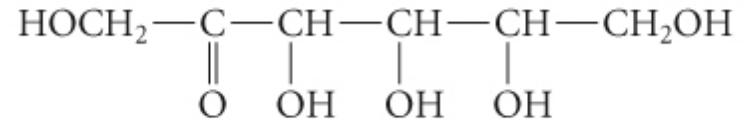
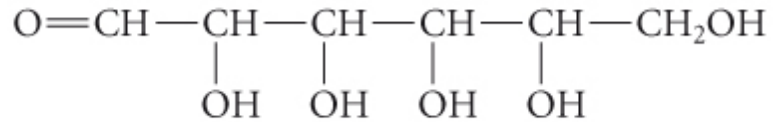


CARBOIDRATI o ZUCCHERI

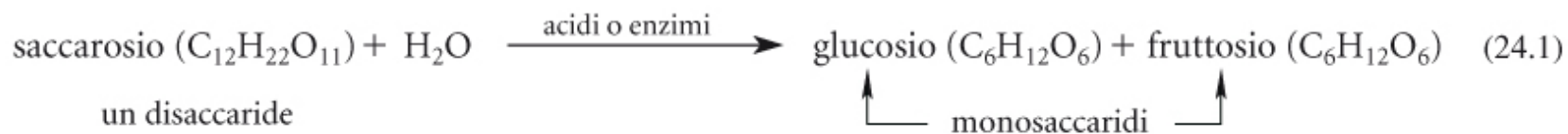
Due comuni strutture di carboidrati:



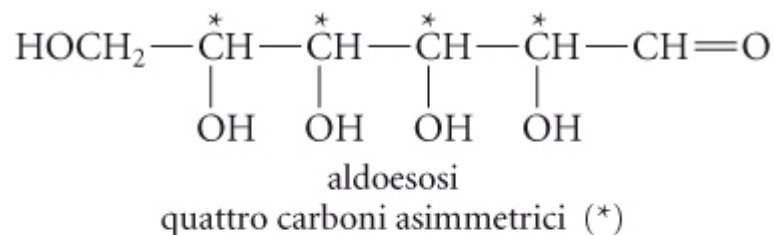
un *aldoso* (gruppo carbonilico aldeidico)
un *esoso* (sei atomi di carbonio)
un *aldoesoso* (combinazione delle due
classificazioni)

un *chetoso* (gruppo carbonilico chetonico)
un *pentoso* (cinque atomi di carbonio)
un *chetopentoso* o *pentulosio* (combinazione
delle due classificazioni)





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PROIEZIONI di FISCHER

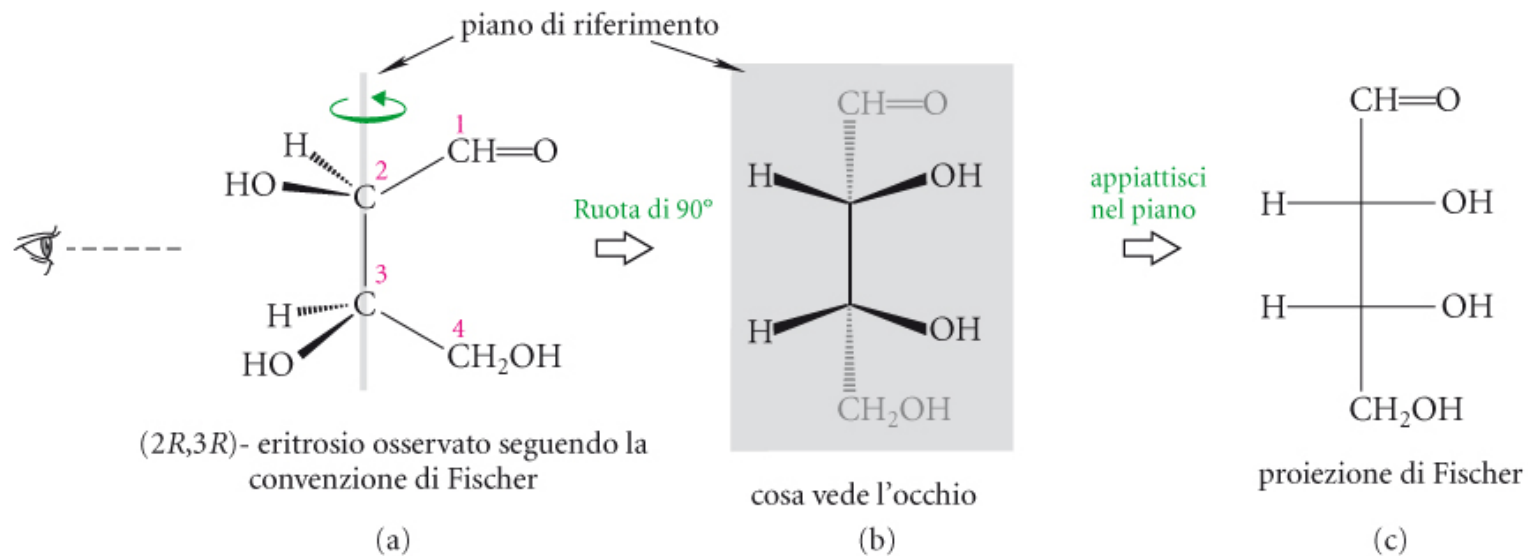


Figura 24.1 Come ottenere una proiezione di Fischer per un aldotetroso. (a) La conformazione eclissata usata per ottenere la proiezione, con il piano di riferimento perpendicolare alla pagina. (b) Vista della conformazione di (a) dal lato dell'osservatore. Il piano di riferimento è adesso il piano della pagina. I gruppi dietro al piano sono mostrati in grigio. (c) Proiezione di Fischer. I carboni asimmetrici sono localizzati all'intersezione tra le linee verticali e orizzontali.

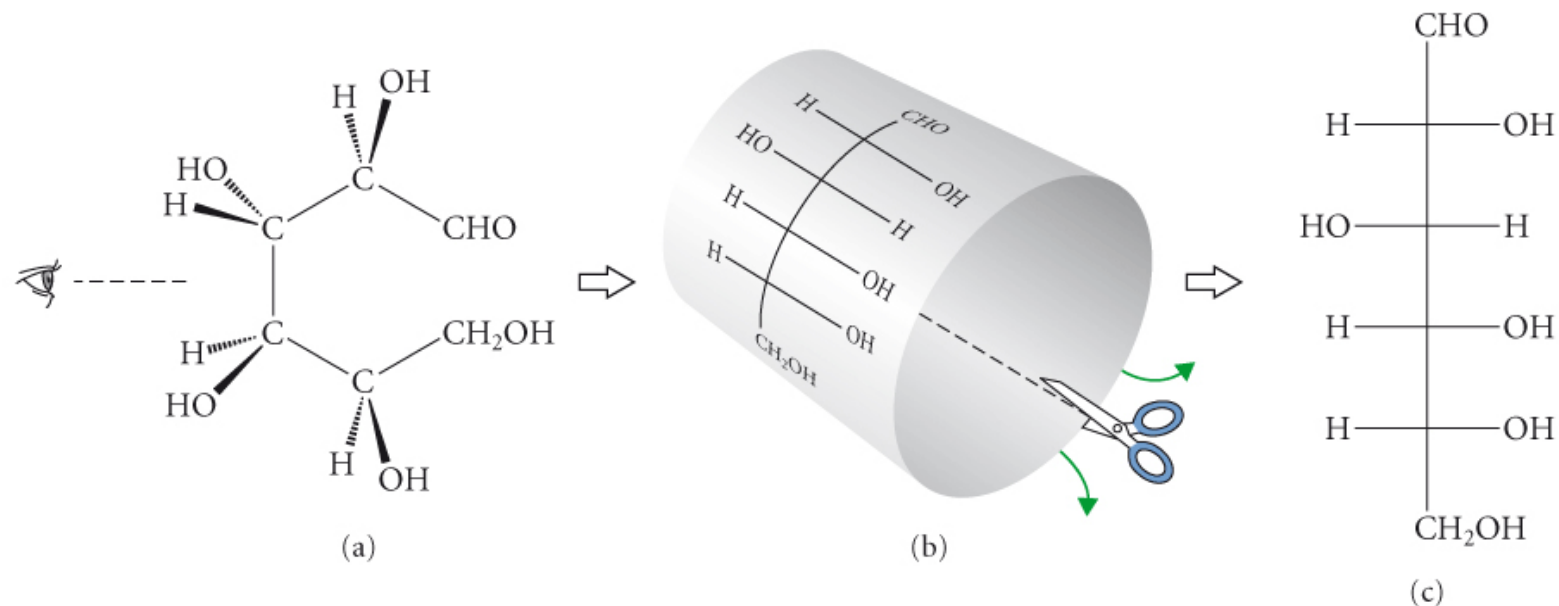
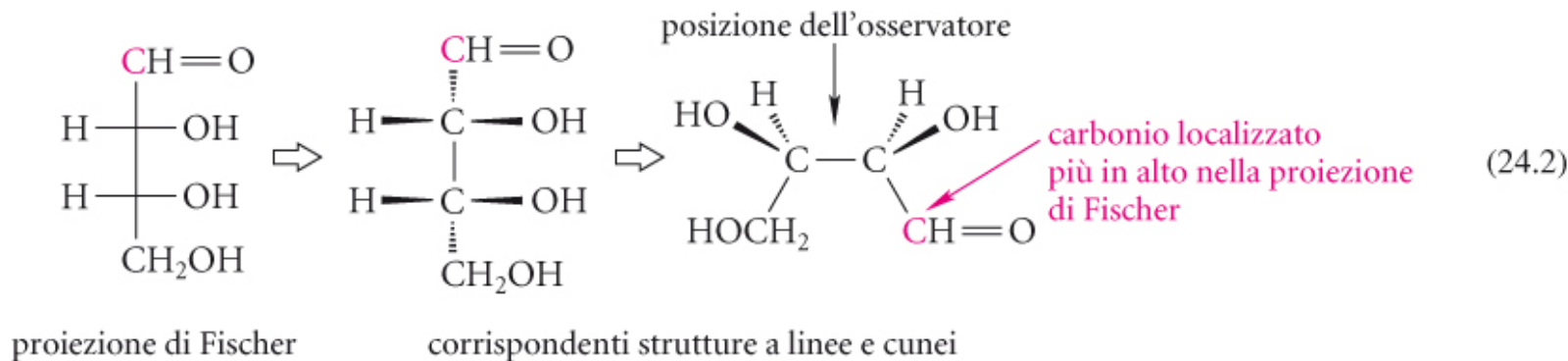
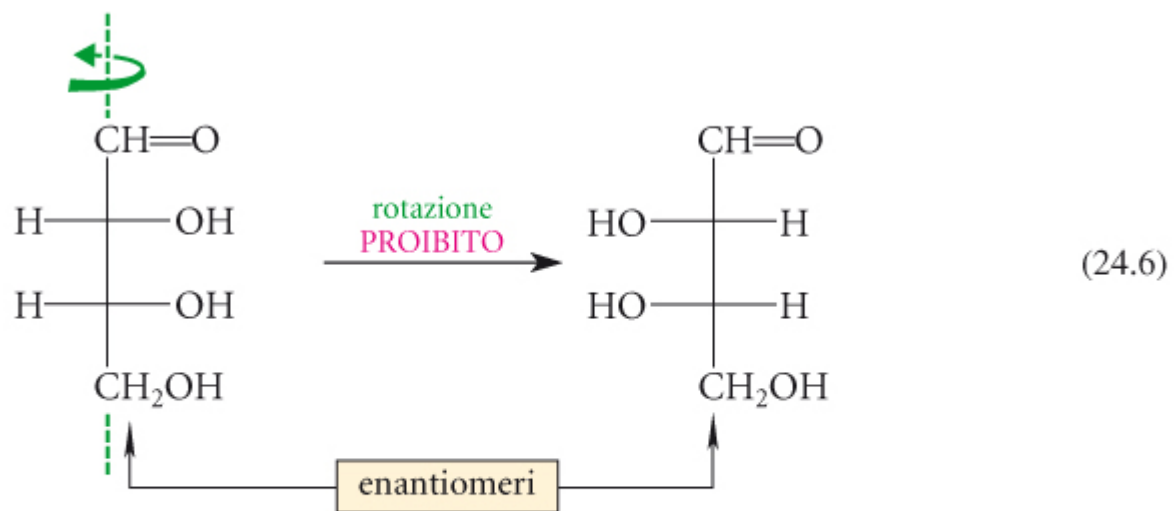
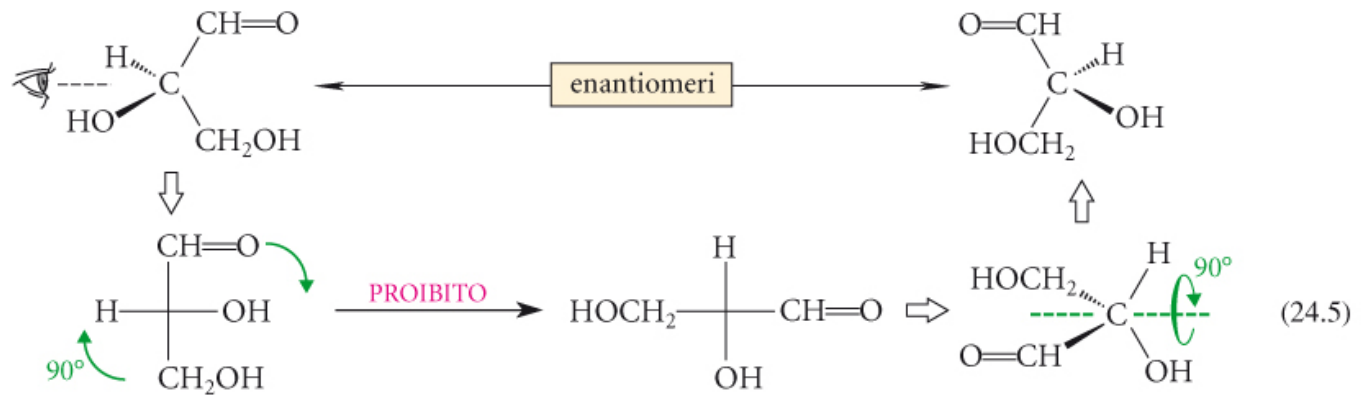
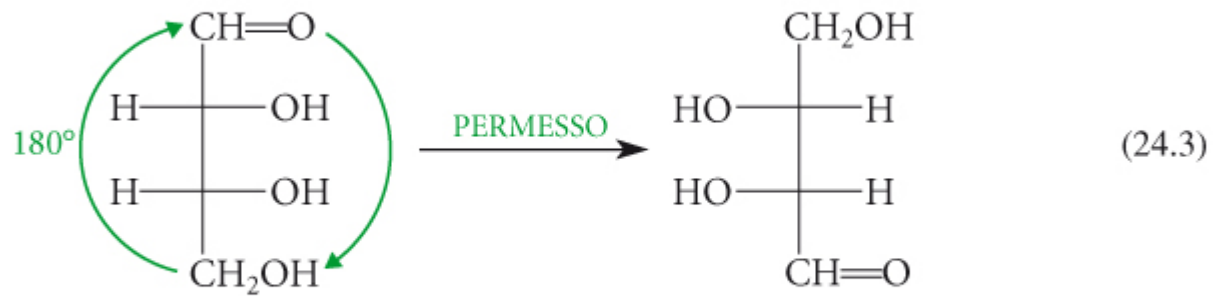
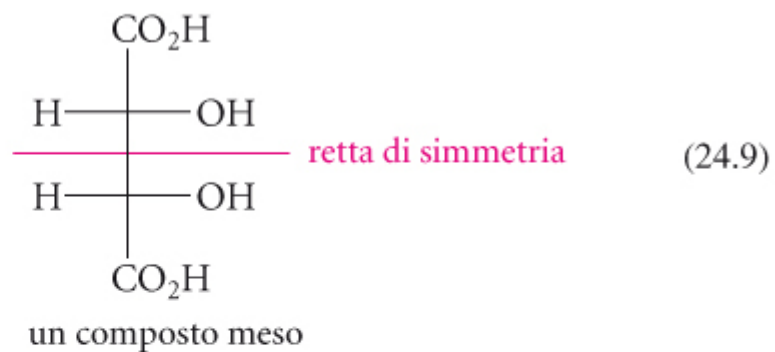
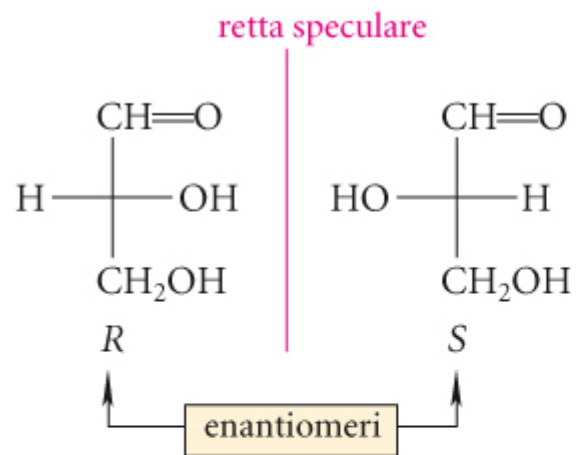


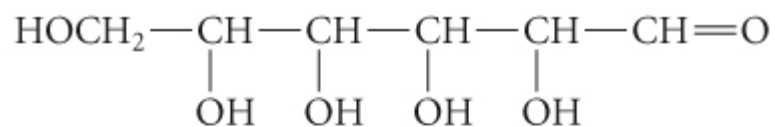
Figura 24.2 Come ottenere la proiezione di Fischer del D-glucosio, l'enantiomero naturale di questo zucchero. (a) La conformazione eclissata viene osservata con la catena carboniosa orientata verticalmente, ma ricurva, che si allontana dall'osservatore e con i legami orizzontali proiettati verso l'osservatore. (b) La molecola così disposta viene proiettata su un cilindro ricurvo immaginario. (c) Tagliando mentalmente il cilindro ed appiattendolo, si ottiene la proiezione di Fischer.







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aldoesosi
 $2^4 = 16$ stereoisomeri



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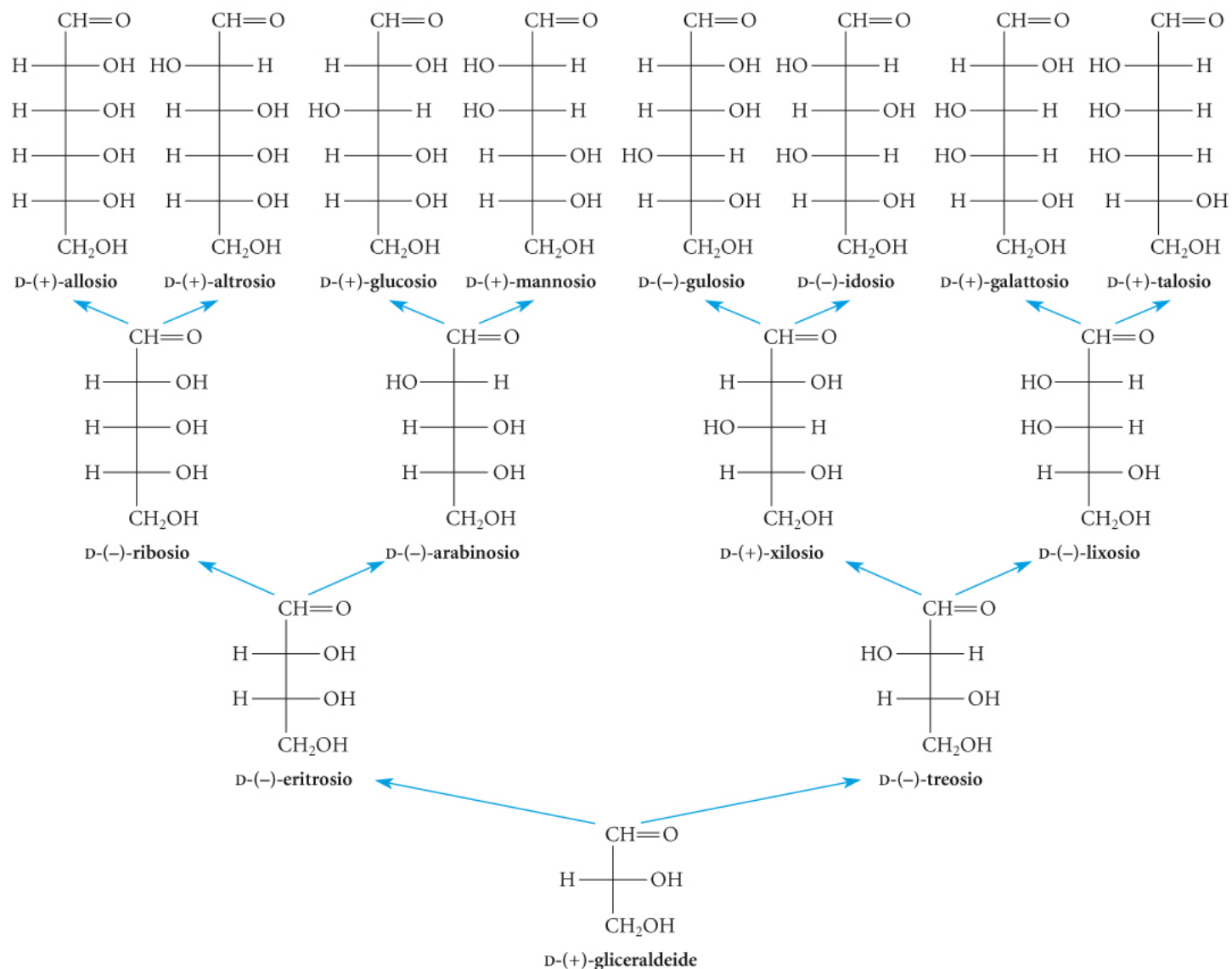
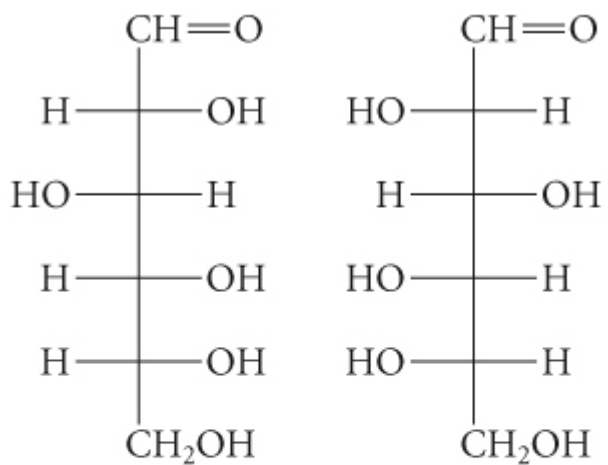
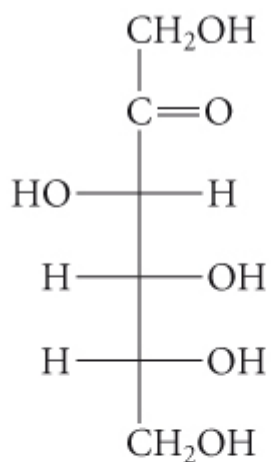
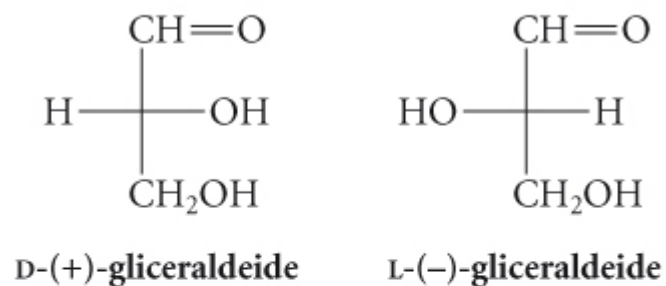


Figura 24.3 3 La serie D degli aldosi. Ciascun composto mostrato ha un enantiomero nella serie L. Le frecce blu mostrano come gli aldosesi siano correlati dalla sintesi di Kiliani-Fischer (Par. 24.9).



enantiomeri del glucosio

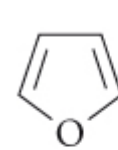
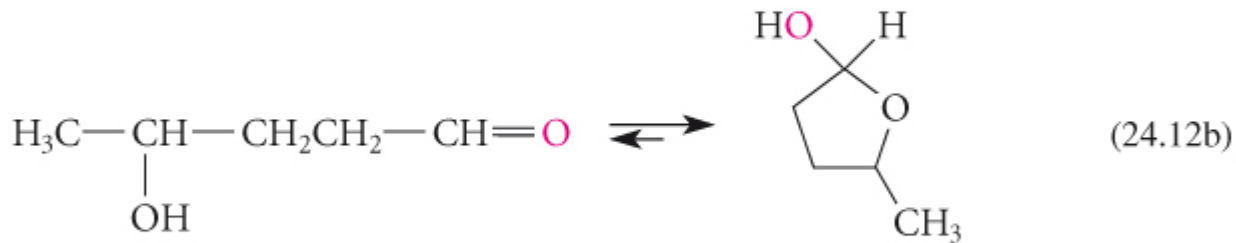
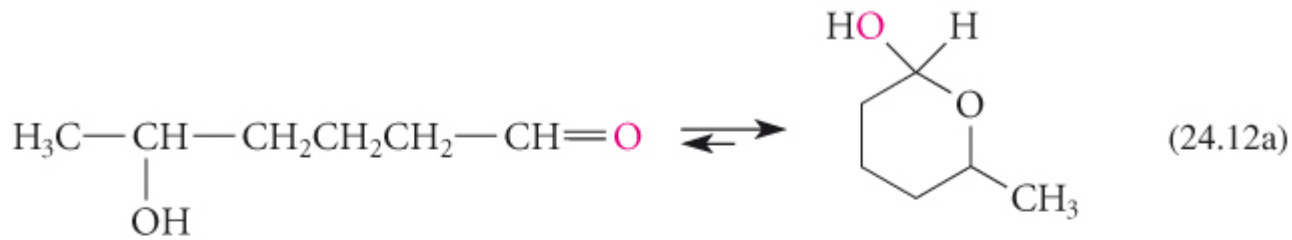


D-fruttosio

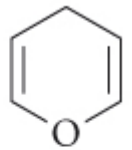


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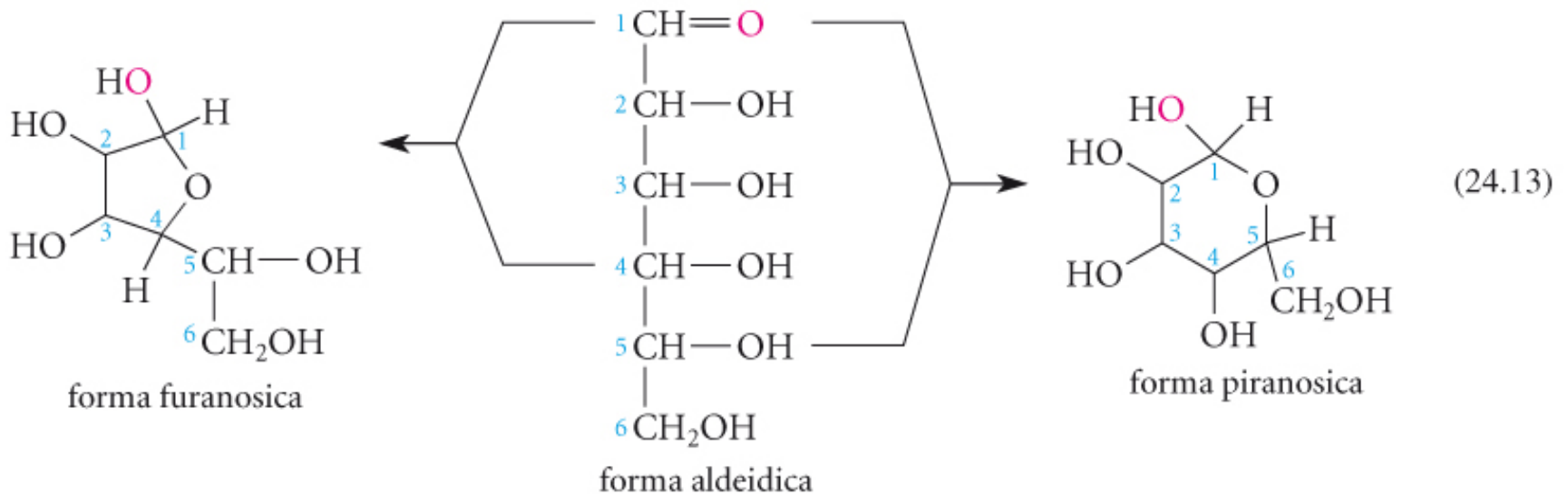
Emiacetali ciclici



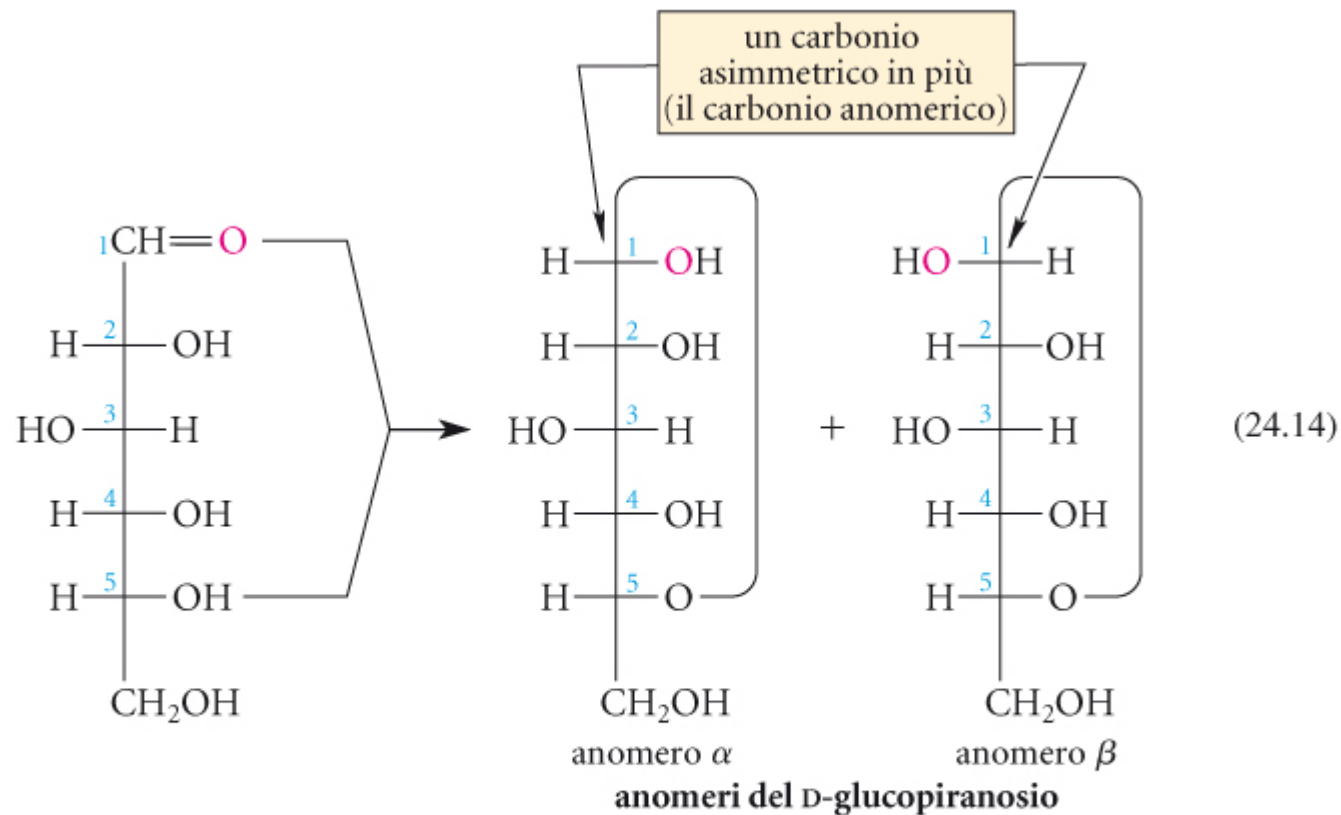
furano

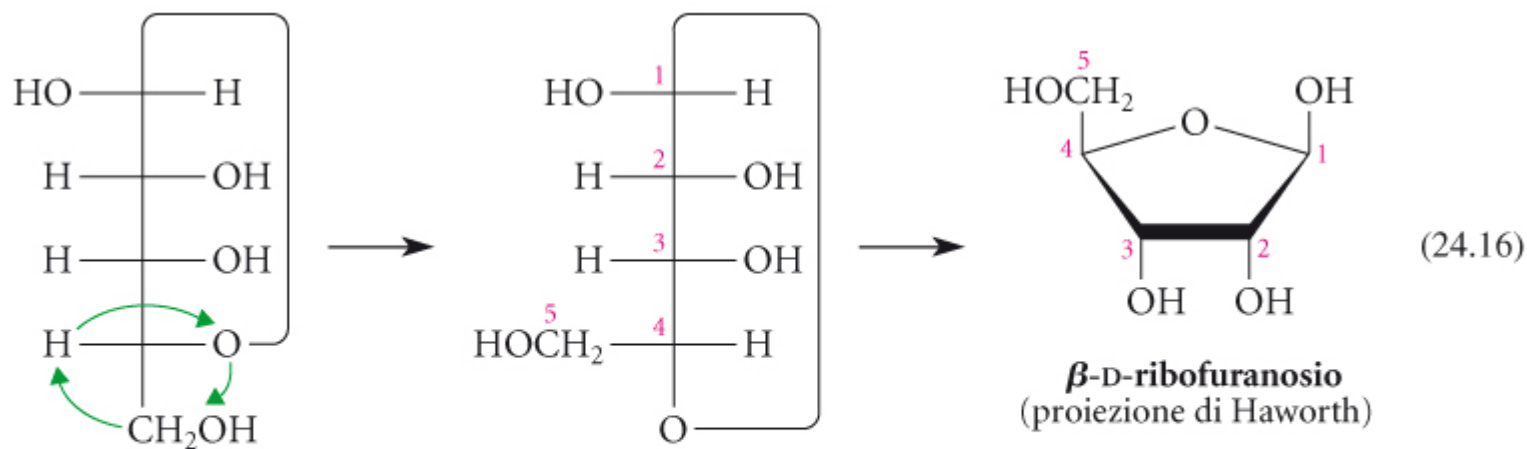
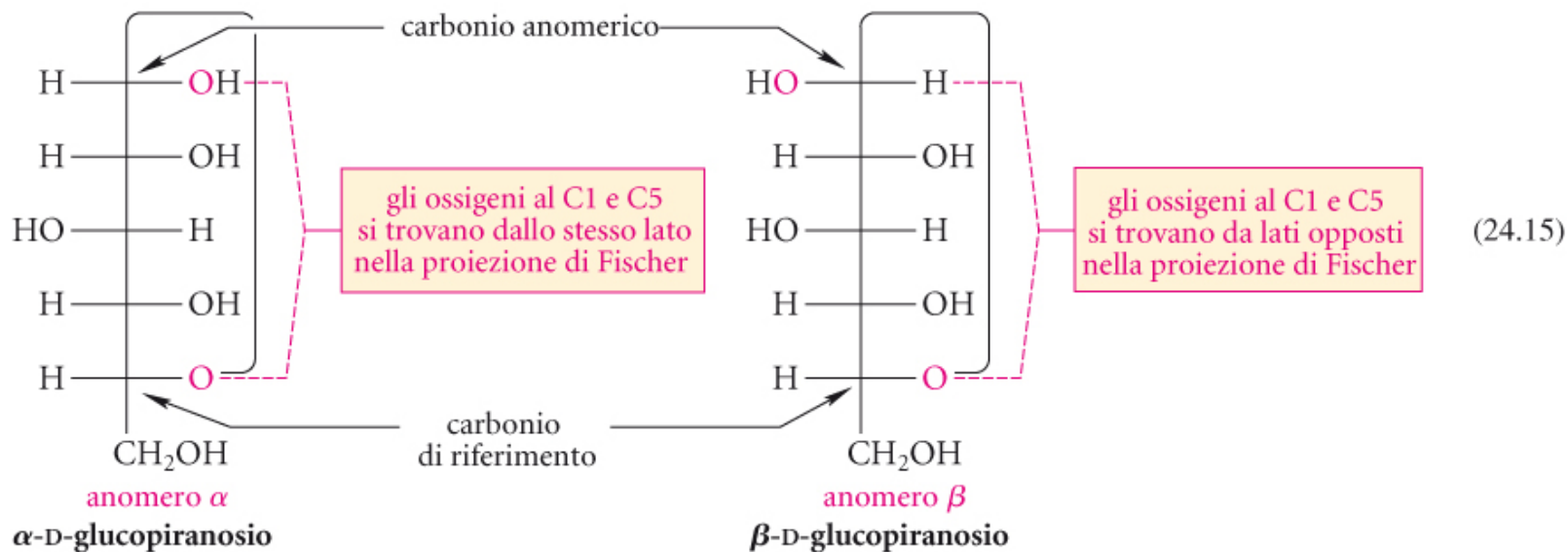


pirano

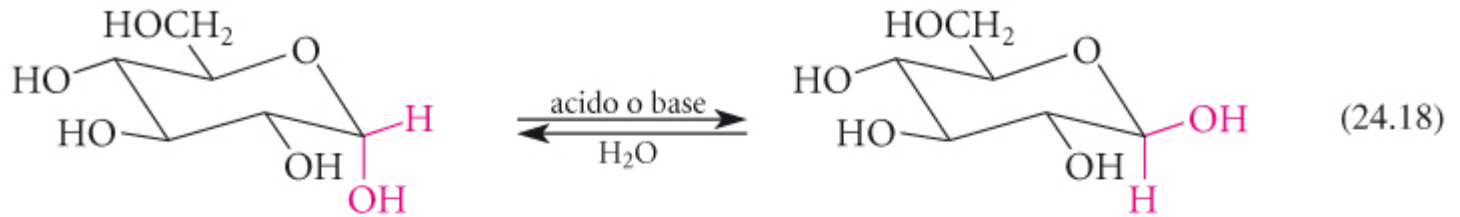


CARBONIO ANOMERICO ed EPIMERI





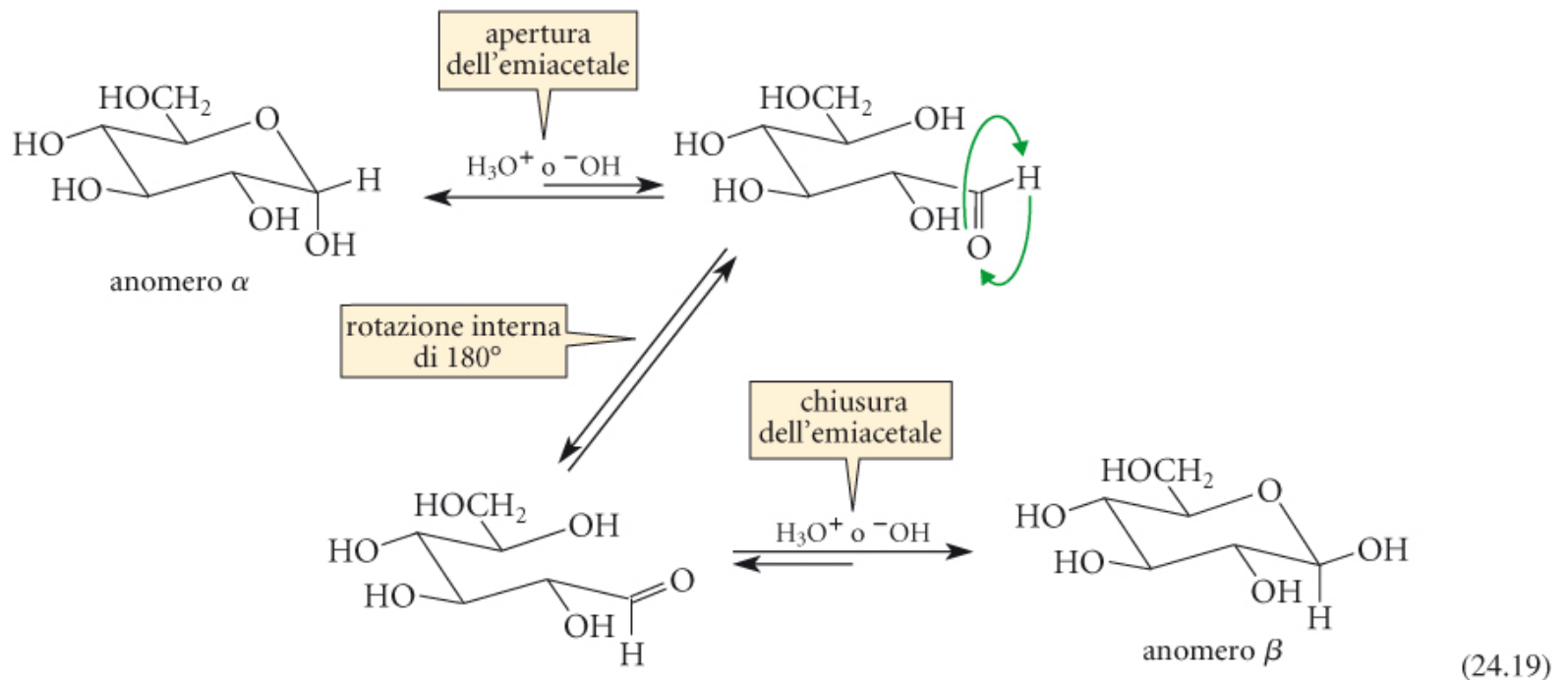
MUTAROTAZIONE



anomero α
 $[\alpha]_D = +112 \text{ gradi mL g}^{-1} \text{ dm}^{-1}$

anomero β
 $[\alpha]_D = +18.7 \text{ gradi mL g}^{-1} \text{ dm}^{-1}$

miscela all'equilibrio: $[\alpha]_D = +52.7 \text{ gradi mL g}^{-1} \text{ dm}^{-1}$



(24.19)

Fruttosio

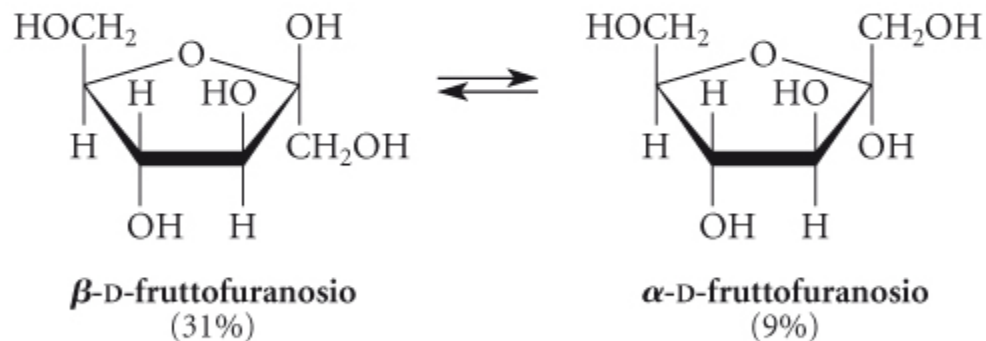
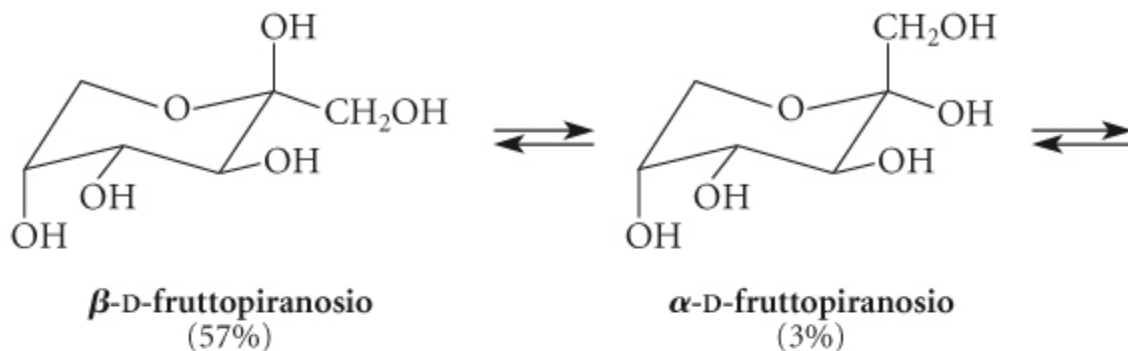
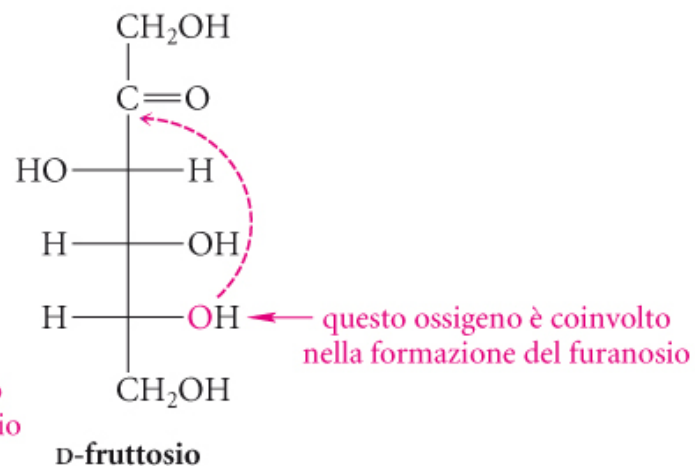
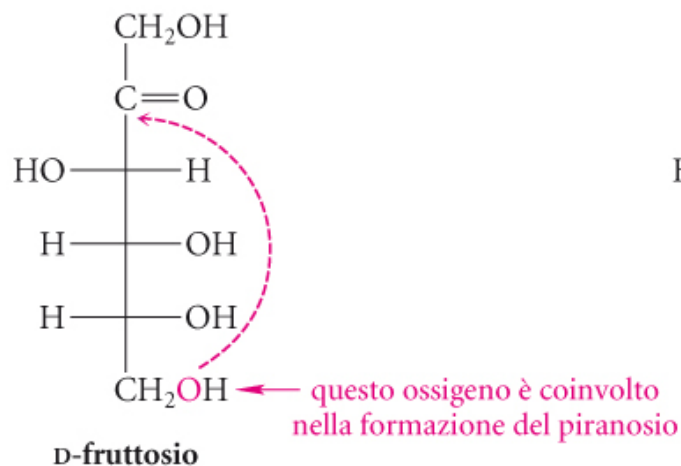


TABELLA 24.1 Composizioni dei monosaccaridi all'equilibrio in soluzione acquosa a 40°C

Zucchero	Percentuale all'equilibrio				Aldeide o chetone
	Piranosio		Furanosio		
	α	β	α	β	
D-glucosio	36	64	tracce*		0.003
D-galattosio [†]	27–36	64–73	tracce		tracce
D-mannosio	68	32	tracce	0	tracce
D-allosio	18	70	5	7	
D-altrosio	27	40	20	13	
D-idosio [‡]	39	36	11	14	
D-taloso	40	29	20	11	
D-arabinosio [§]	63	34	3		
D-xilosio	37	63			
D-ribosio	20	56	6	18	0.02
D-fruttosio	0–3	57–75	4–9	21–31	0.25

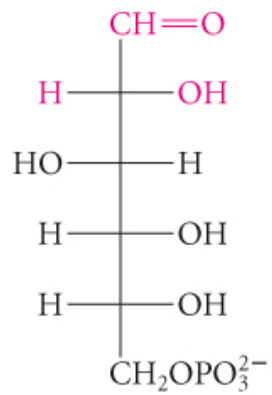
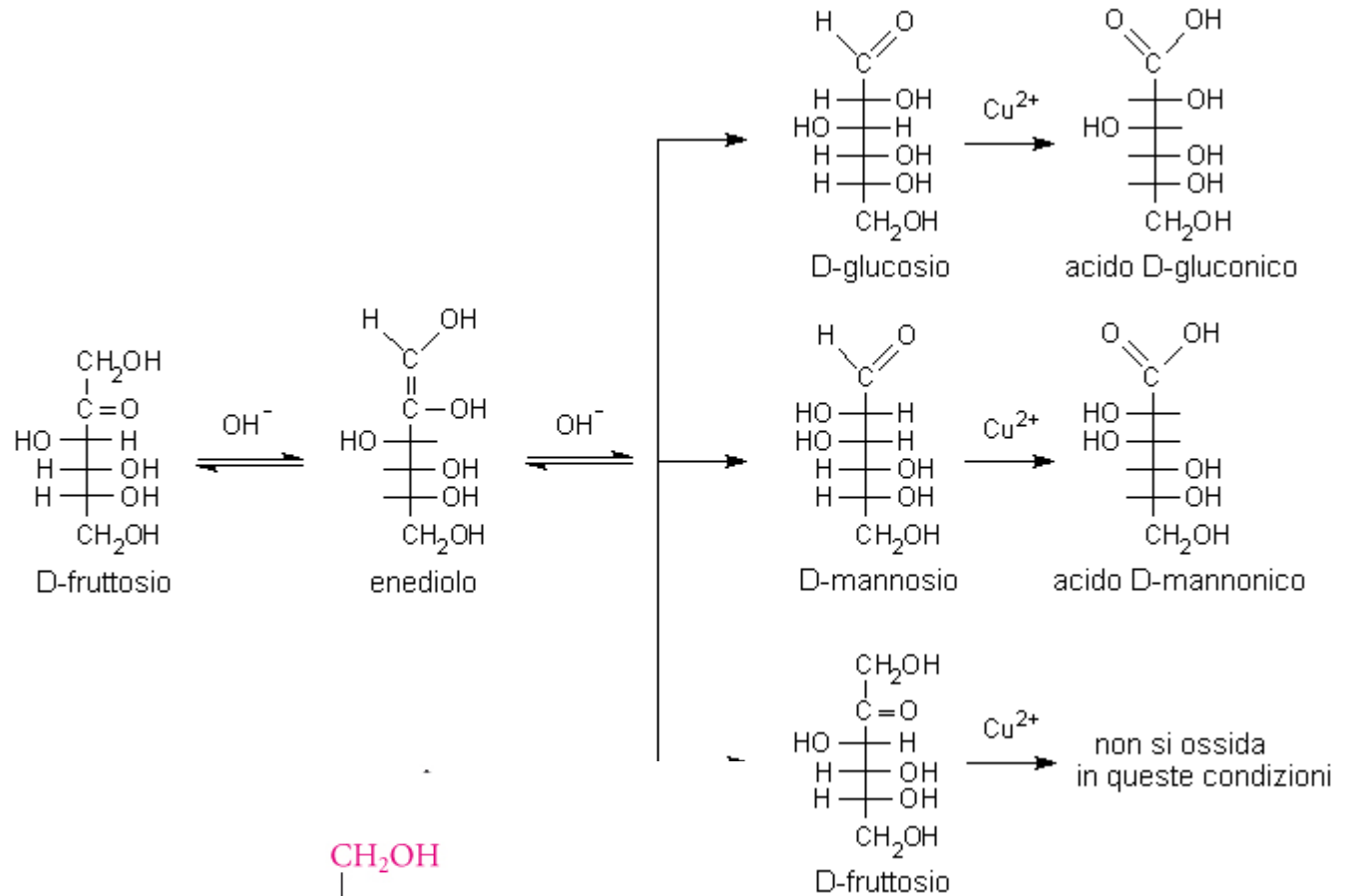
** In soluzione acquosa al 10% di diossano, il glucosio contiene lo 0.1-0.2% di ciascun furanosio.

[†] A 25°C, il galattosio contiene il 29% di α -piranosio, il 64% di β -piranosio, il 3% di α -furanosio e il 4% di β -furanosio.

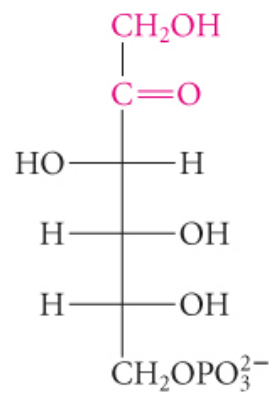
[‡] 25 °C

[§] A 25°C, l'arabinosio contiene il 60% di α -piranosio, il 35% di β -piranosio, il 3% di α -furanosio e il 2% di β -furanosio.

Fruttosio: zucchero riducente??



D-glucosio-6-fosfato isomerasi (enzima)

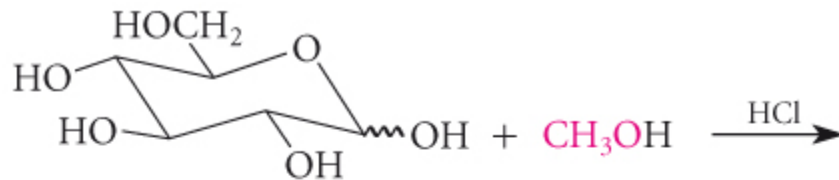


(24.24)

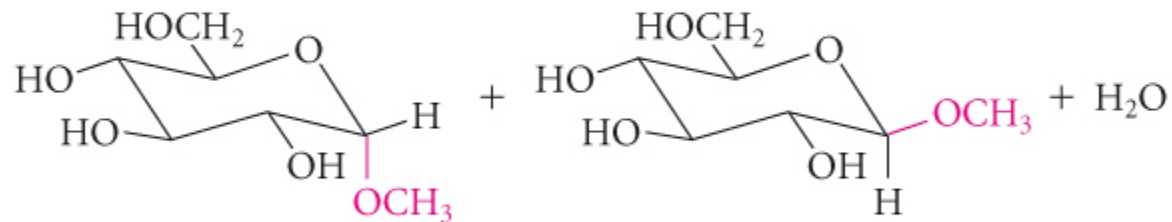
D-glucosio-6-fosfato

D-fruttosio-6-fosfato

Glicosidi: carboidrato (forma emiacetalica) + alcol



D-glucosio



metil α -D-glucopiranoside

metil β -D-glucopiranoside

(resa 83–85%; separati per cristallizzazione frazionata)

(24.25)

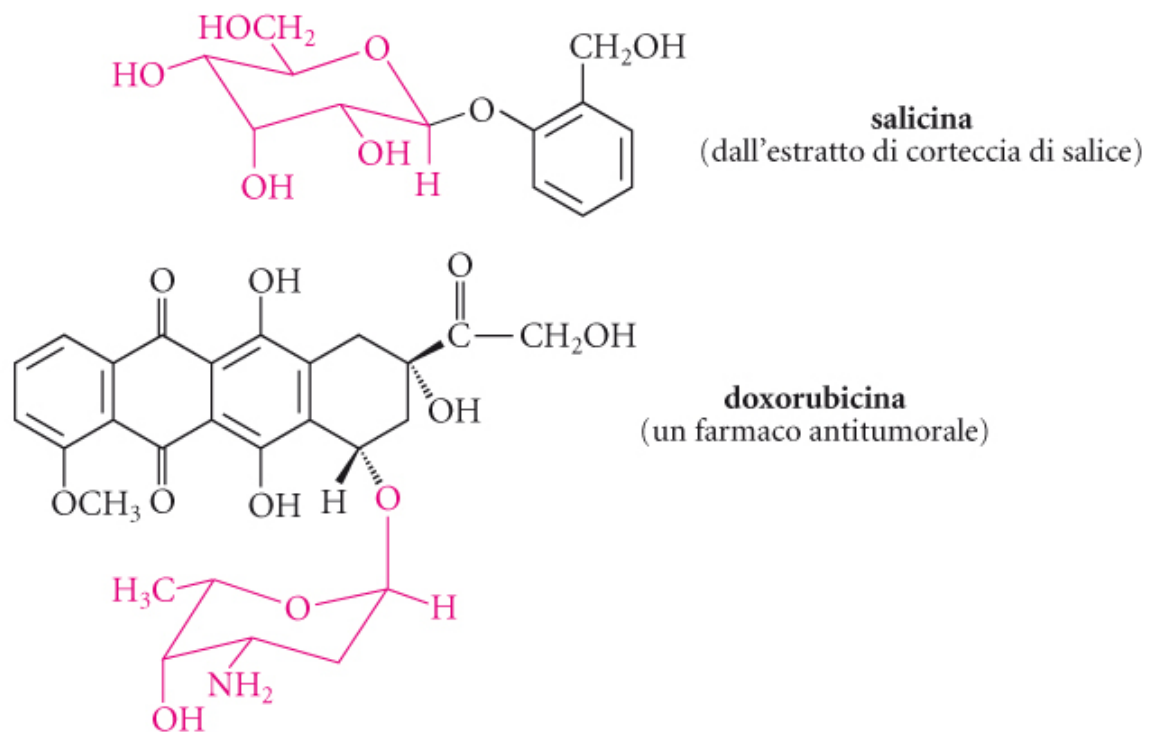
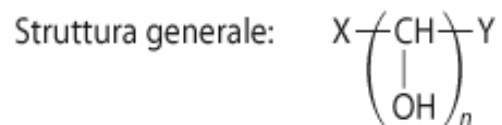


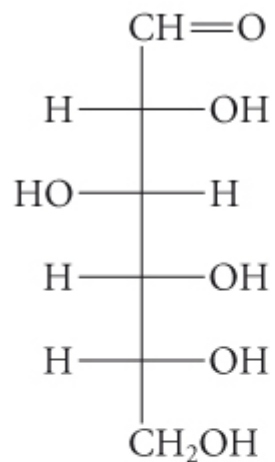
Figura 24.4 Due glicosidi naturali di interesse farmaceutico. La parte zuccherina di ciascun glicoside è mostrata in rosso.

TABELLA 24.2 Strutture dei prodotti di ossidazione e riduzione degli aldosi

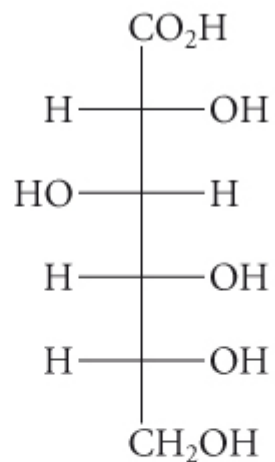


Struttura generale		Nome generale	Esempio per il glucosio
X— =	—Y =		
HOCH ₂ —	—CH=O	aldoso	glucosio
HOCH ₂ —	—CO ₂ H	acido aldonico	acido gluconico
HO ₂ C—	—CO ₂ H	acido aldarico	acido glucarico
HOCH ₂ —	—CH ₂ OH	alditolo	glucitolo
HO ₂ C—	—CH=O	acido uronico	acido glucuronico

Esempi



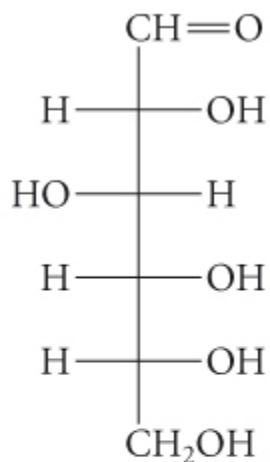
D-glucosio



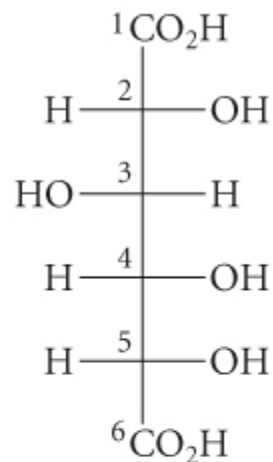
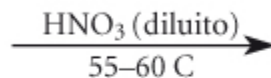
acido D-gluconico

(un acido aldonico;
resa 77-96% come sale con Ca^{2+})

(24.35)



D-glucosio

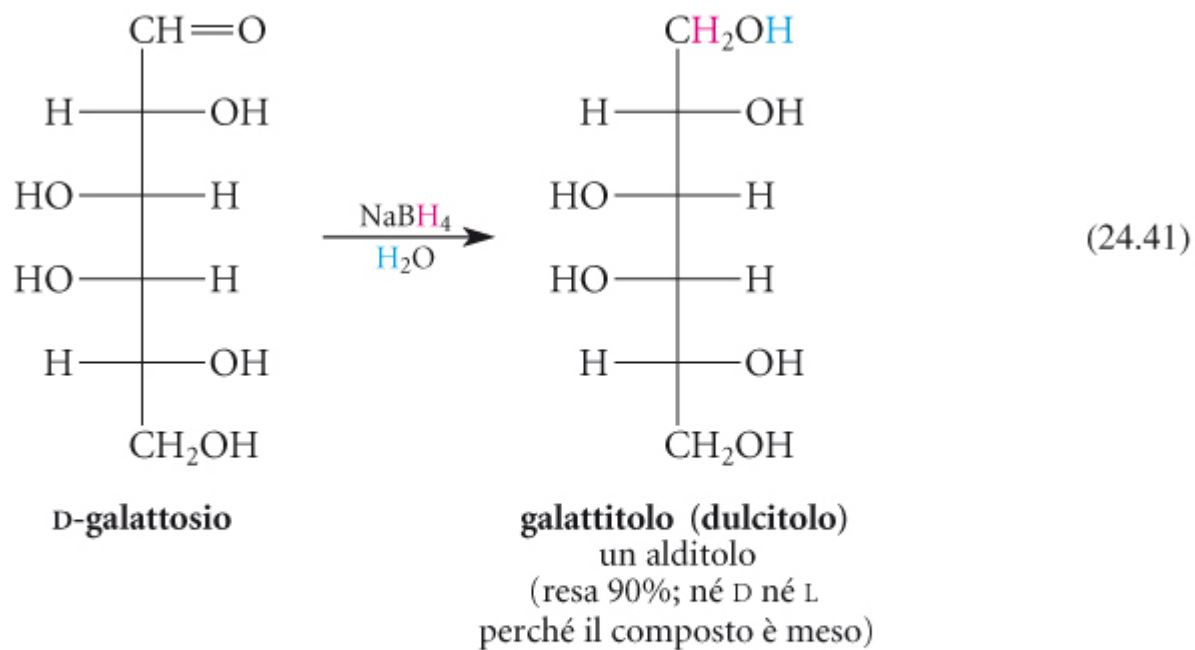


acido D-glucarico

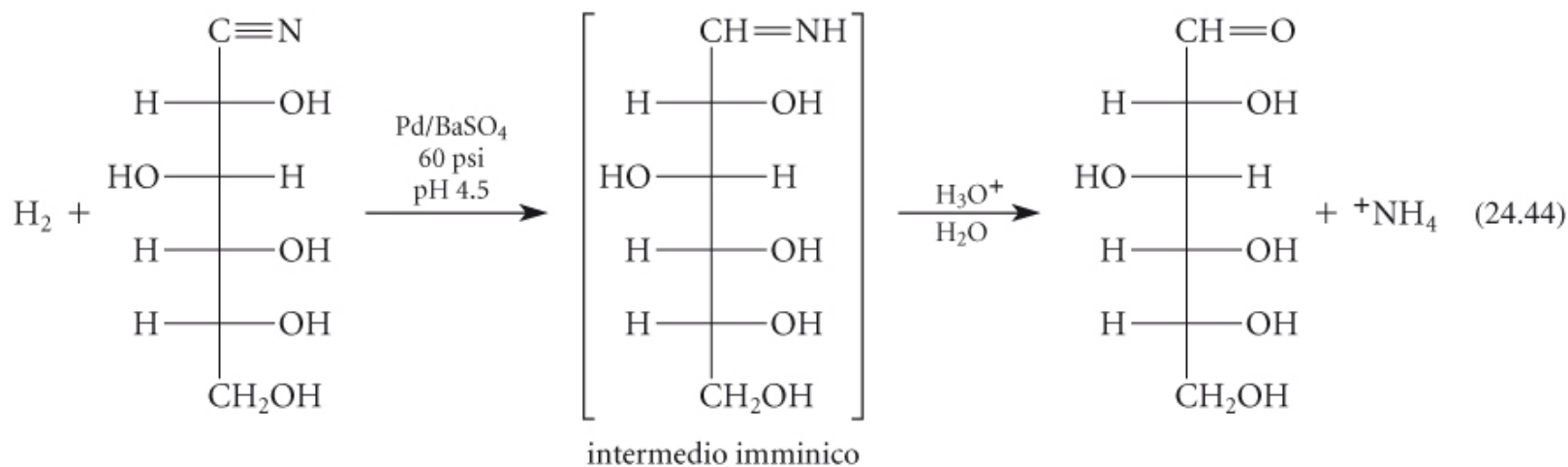
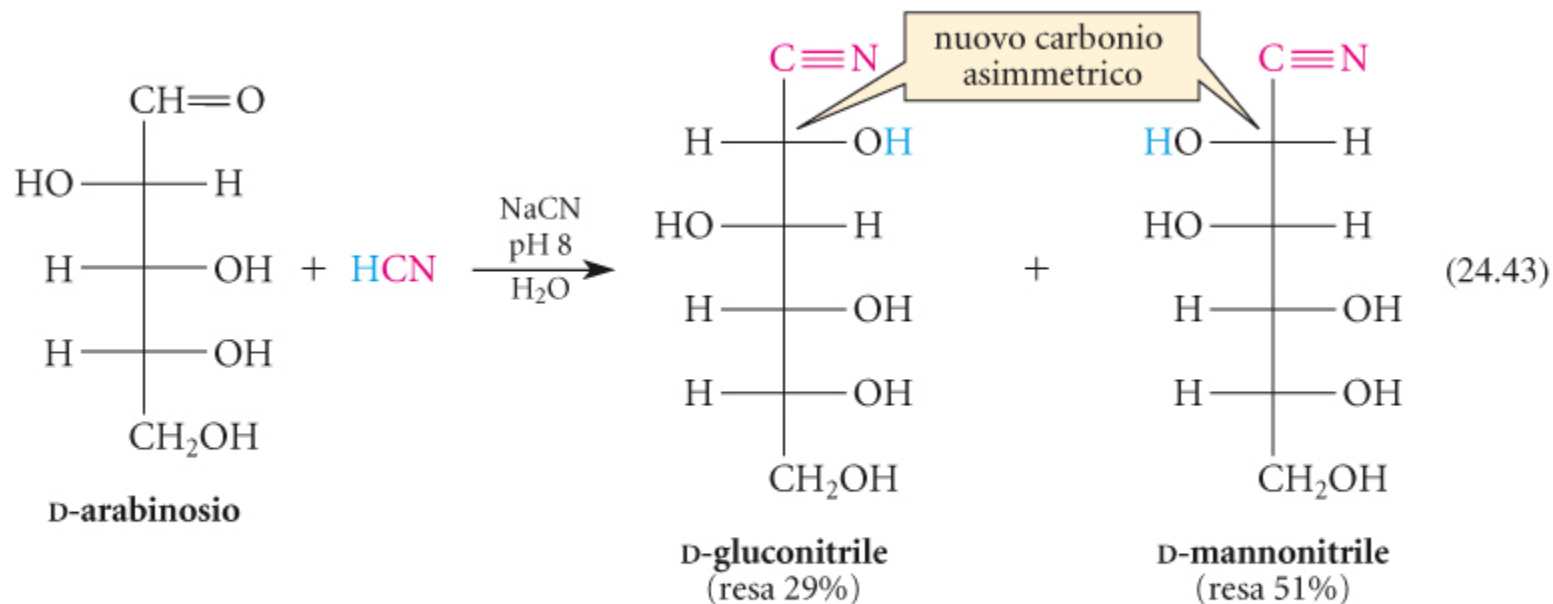
(un acido aldarico)

(resa 41%, isolato come sale con Ca^{2+})

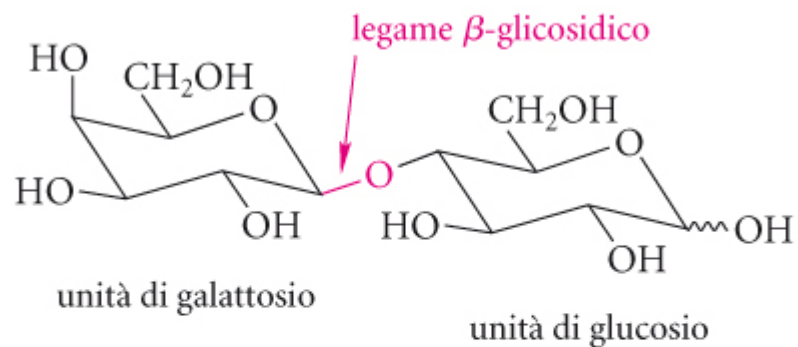
(24.37)



Sintesi di Kiliani-Fischer



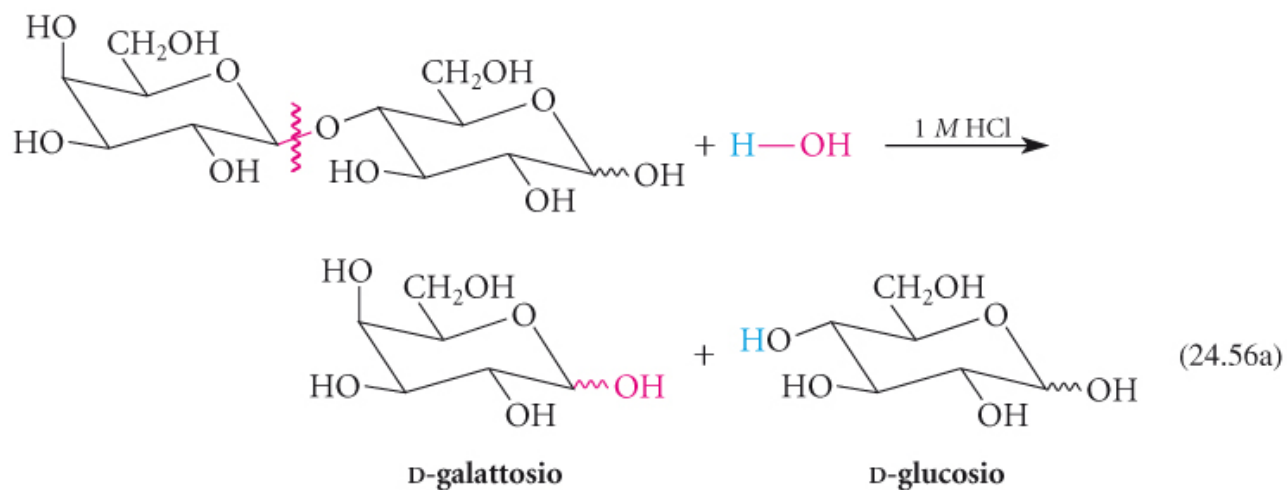
DISACCARIDI



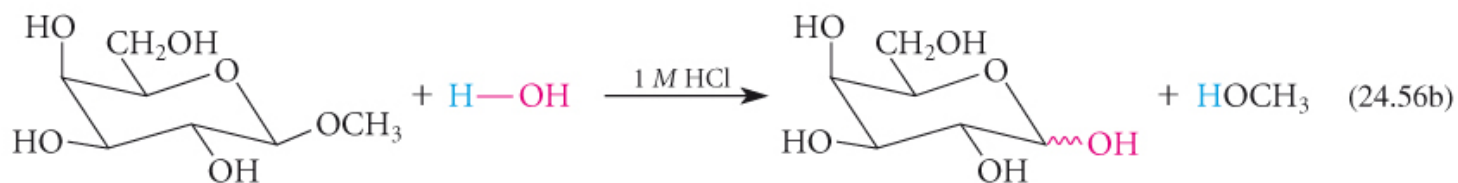
(+)-lattosio o 4-O-(β-D-galattopiranosil)-D-glucopiranosio

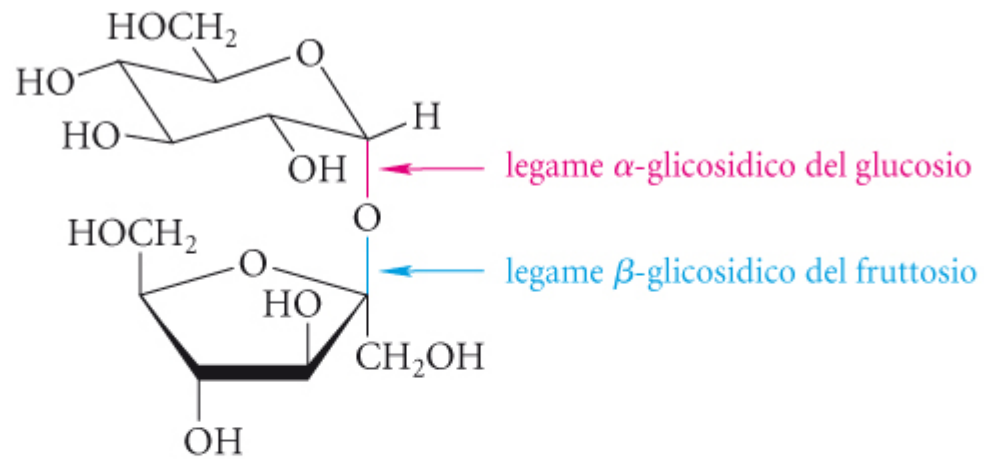


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Confronta:



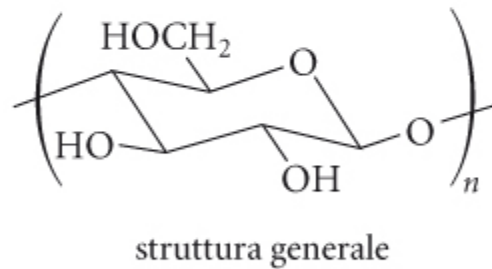
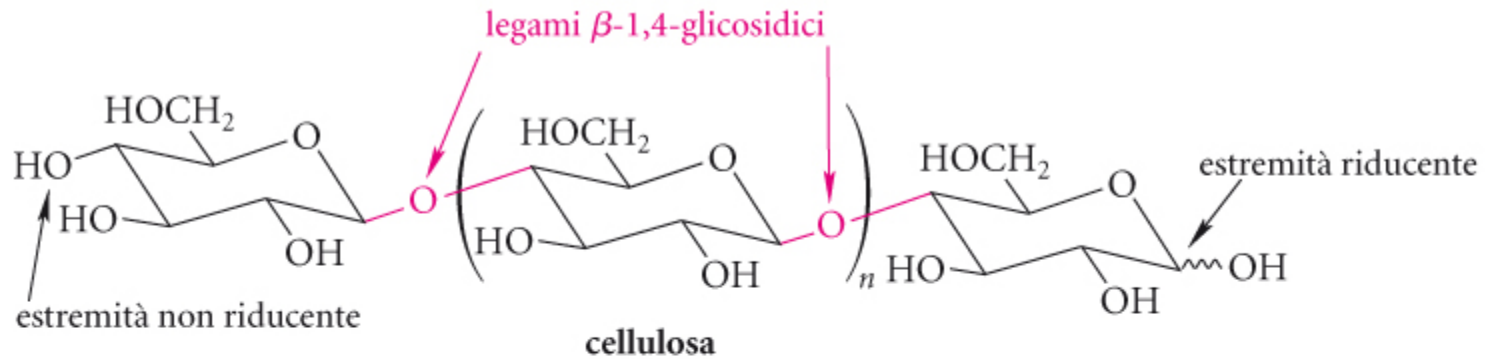


(+)-saccarosio (α -D-glucopiranosil- β -D-fruttofuranoside)

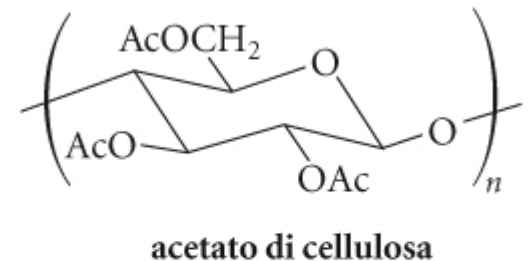


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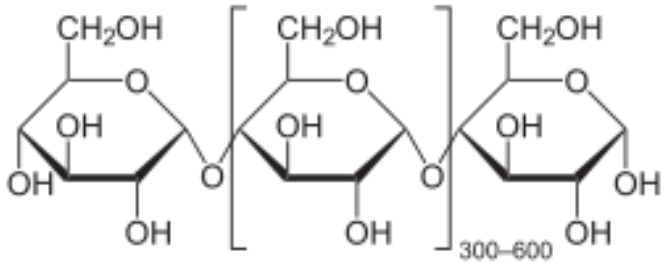
POLISACCARIDI



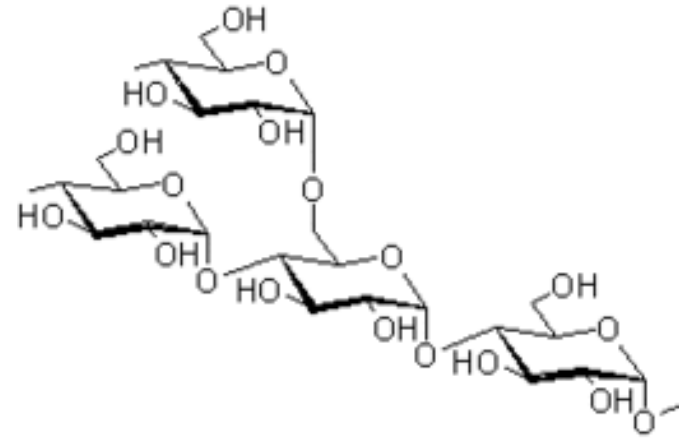
1.



Amido

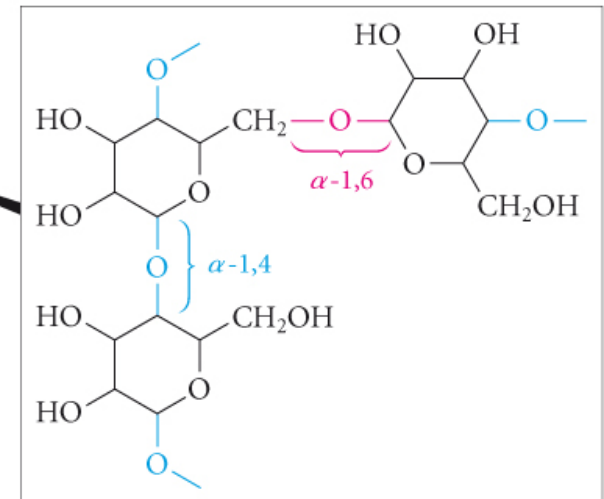
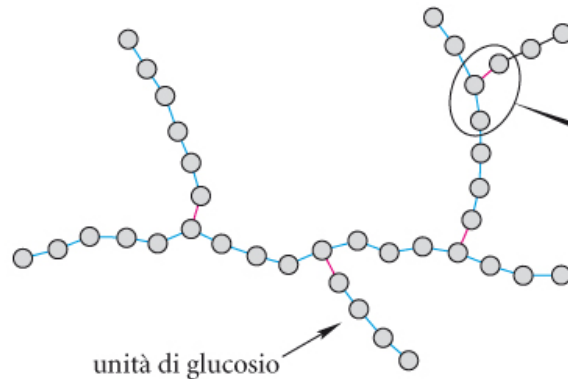
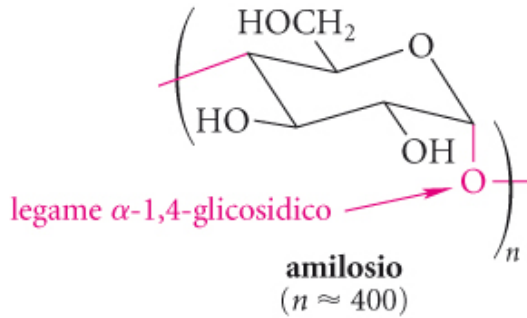


Amilosio (20%)



Amipectina (80%)

Ogni 24-30 unità vi è una ramificazione



una ramificazione dell'amipectina