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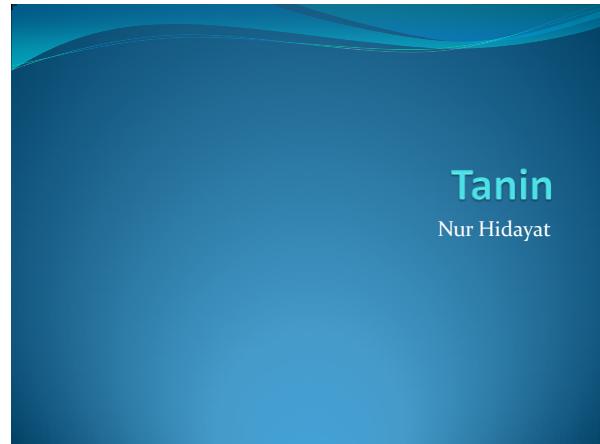
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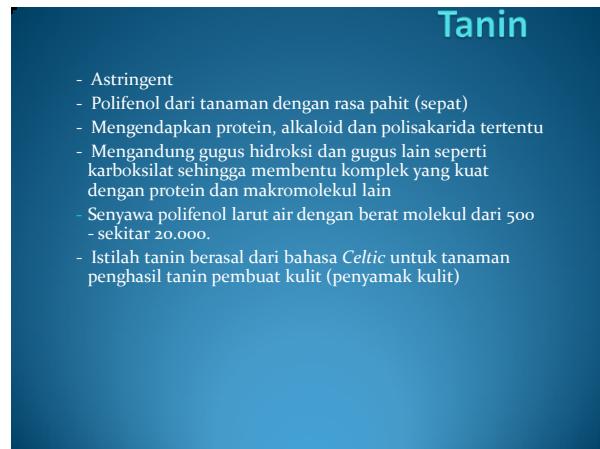
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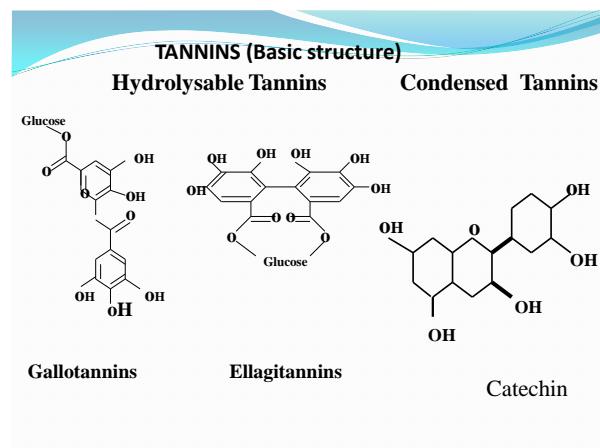
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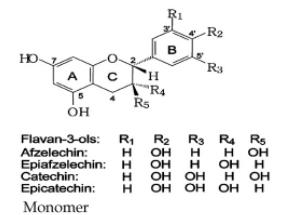
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## Tanin Terkondensasi

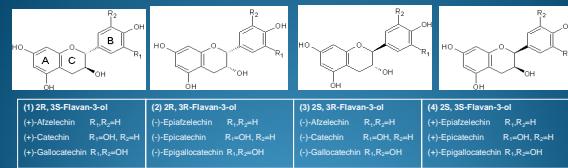
Tanin terkondensi  
(protoantosianidin)  
adalah polimer dari  
flavonoid

Walaupun jalur  
biosintesis flavonoid  
telah dimengerti dengan  
baik, namun tahapan  
yang mengarah kepada  
kondensasi dan  
polimerisasi belum  
banyak dielusidi



Tanin terkondensi (Condensed tannin) adalah berdasarkan senyawa flavan-3-ols (-)-epikatekin dan (+)-catekin

### Struktur dari flavan-3-ols 1, 2 dan ent-flavan-3-ols 3,



## Tanin Terkondensasi

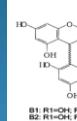
## Tanin Terkondensasi

Penambahan gugus fenol ketiga pada cincin B menghasilkan epigalokatekin dan galokatekin  
Tannin terkondensi dicirikan dengan adanya ikatan karbon-karbon (C-C) antara atom C8 pada cincin A dan C4 pada cincin B, tapi juga ada yang telah ditemukan dengan ikatan rangkap antara C6-C4

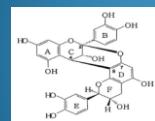
- Empat jenis pasangan (coupling) ditunjukkan oleh dimer yang berupa:
1. Epikatekin-(4β-8)-catekin
  2. Epikatekin-(4β-8)-Epikatekin
  3. Katekin-(4β-8)-catekin
  4. Katekin -(4β-8)-Epikatekin

## Tanin Terkondensasi

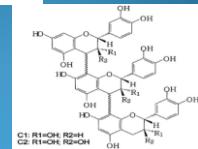
Contoh Dimer C4-C8, C4-C6 dan Trimer. Polimer linear C4-C8 paling banyak ditemukan dibanding plimer C4-C6 ataupun polimer bercabang C4-C6 dan C4-C\*



B1: R1=OH; R2=H; R3=H; R4=OH  
B2: R1=OH; R2=H; R3=OH; R4=H



C1: R1=OH; R2=H  
C2: R1=OH; R2=OH



## Tanin Terkondensasi

Walaupun istilah tanin terkondensasi luas digunakan untuk menunjukkan polifenol dari flavonoid, secara struktur istilah proantosianidin lebih banyak diterima

Proantosianidin adalah senyawa yang menghasilkan pigmen antosianidin dengan pemutusan oksidatif (bukan hidrolisis) pada alkohol panas melalui reaksi butanol asam

Polimer dari katekin dan epikatekin menghasilkan sianidin sehingga dinamakan dengan prosianidin  
Polimer dari galokatekin dan epigalokatekin menghasilkan delfinidin

Polimer dari flavan-3-ol yang mempunyai monosubstitusi yang biasanya jarang menghasilkan pelargonidin

## Tanin Terkondensasi

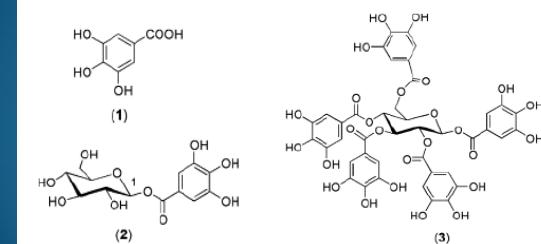
Kelompok yang penting pada tanin terkondensasi adalah polimer dari 5-deoksi-flavan-3-ols, percabangan biasanya umum pada tanin ini disebabkan oleh reaktivitas dari cincin 5-deoksi Flavan-3,4-diols atau leukoantosianidin (perlu dibedakan dengan proantosianidin) adalah monomer flavonoid yang menghasilkan antosianidin ketika dipanaskan dalam asam. Secara kimia sama dengan tanin terkondensasi tetapi senyawa ini tidak berinteraksi dengan protein membentuk kompleks yang mengendap

Flavan 4-ols juga leukoantosianidin, senyawa ini menghasilkan antosianidin melalui reaksi dengan alkohol asam pada suhu kamar

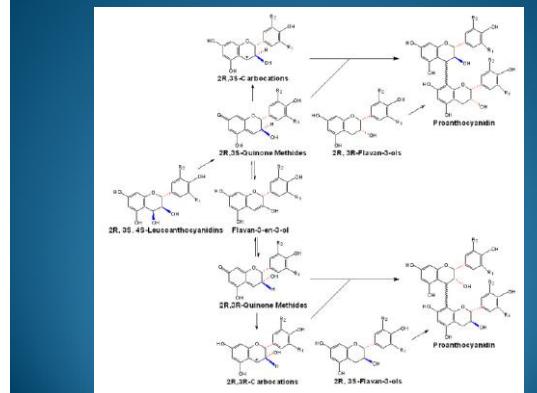
3-deoksiantosianidin ditemukan juga pada sejumlah kecil tanaman

### Tanin Terhidrolisis (Hydrolyzable Tannins)

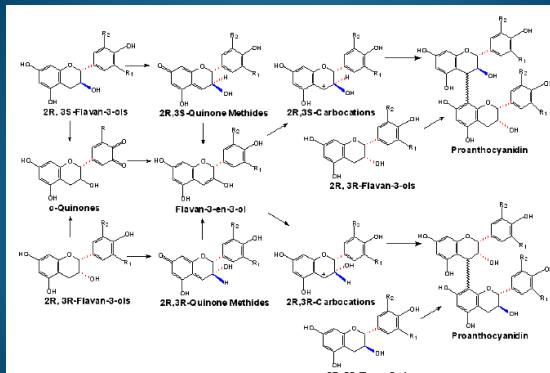
Tanin terhidrolisis adalah turunan dari asam galat (3,4,5-trihidroksi asam benzoat). Asam galat adalah hasil esterifikasi menjadi tiol dan galoil dapat selanjutnya diesterifikasi atau secara oksidatif berikatan menghasilkan tanin terhidrolisis yang lebih komplek

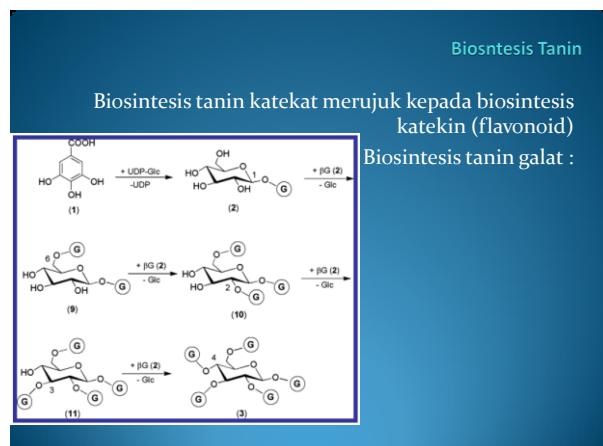
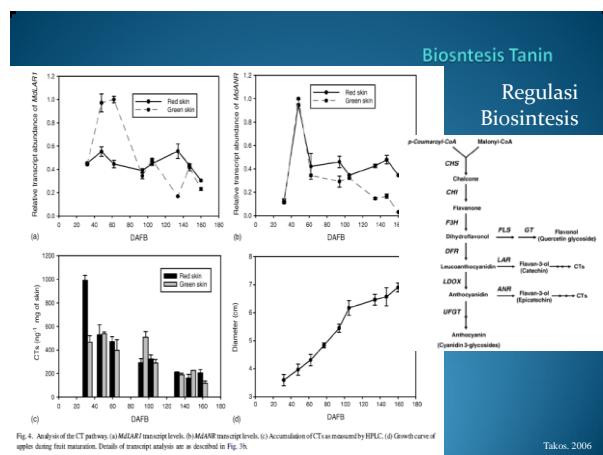
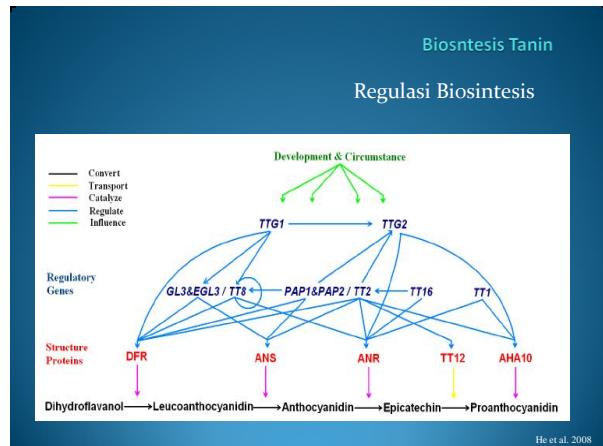


### Biosintesis Tanin

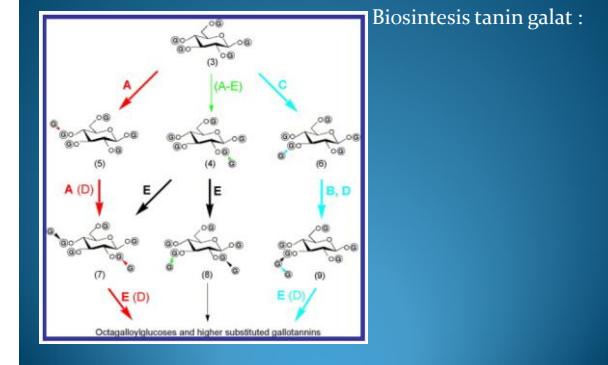


### Biosintesis Tanin



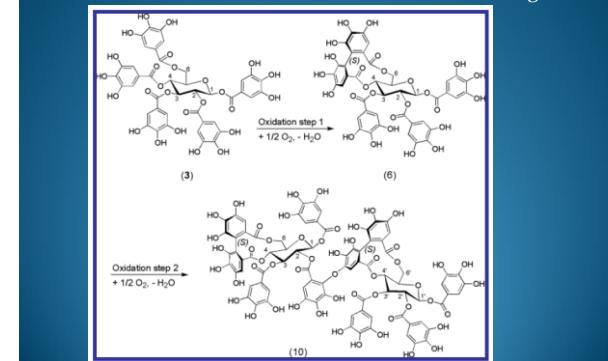


## Biosintesis Tanin



## Biosintesis Tanin

### Biosintesis tanin galat :



## Sumber Tanin

Appl Microbiol Biotechnol (2008) 78:189–199

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Table 1 Sources of main ellagitannins

Ellagitannins	Fuente vegetal	References
Vascaglin, castaglin and valones	<i>Quercus</i> sp.	Iri et al. 2000; Huang et al. 2005; Isaza et al. 2004
Nobotannin G, K, P,G, R,S and T; bretolin B, nobotannin A, B, F, β-glucogallin, pedunculagin, 4-(6-O-HHDG)-glucopyranose, malatharin D, pterocaryann C, (1A,6-O-digalloyl-2,3-O-HHDG)-β-D-glucose), Cassuricin (1-O-galloyl-2,3,4,6-O-bisHHDG-β-D-glucose)	<i>Monochaetum multiflorum</i>	
Nobotannin O and P; Stachyurin, Casuarin, Madimilin B, Nobotannin A, B, D, F, G, J and M, Pedunculagin, Cassuricin	<i>Tibouchina multiflora</i>	Yoshida et al. 1999
Thomannianins A and B	<i>Thomningia sanguinea</i>	Oltani et al. 2000; Mullen et al. 2003
Ellagic acid -4-arabinose, Sanguin H-6, Sanguin H-10, Lambertian C, ellagic acid-4-acetylbylyose, ellagic acid-4-acetylbarbutoric	<i>Rubus</i> sp.	
Jolkinin, Geranin, Contaglin, Capnuspin, Putranjivin, Helioscapin B, Iridin, Geranin, Contaglin, Capnuspin, Putranjivin, Helioscapin B, Caplinin D, and D <sub>2</sub> , Woodfordin C, Mirycyrin, Tellimgrandin II, Geranthin B, Phyllanthanobains A, B and F, Contaglin, 1-(3,12,3,6-tetra-O-galloylglucosyl)-chelidonic acid, Elaeo-carpisin, punicalin, mallowin, Putranjivin A, Ellagic acid 4-O-α-4-hamnosylarene, 6-O-galacto(α/β)-d-glucopyranose, 6-O-galloyl-2,3,4-hexahydroxyphenyl-4-O-galacto(α/β)-d-glucopyranose, contaglin, 3,3'-di-O-methyl ellagic acid, 3'-O-methyl-3,4-methylenedioxy ellagic acid, punicaetin D, punicalin, punicatin, 2-O-galloylpunicalin, delphinic acid rhamnosyl (1-4) glucopyranose y 5-galloylpunicacortin D	<i>Euphorbia jolkinii</i> <i>Croton lechleri</i> <i>Phyllanthus emblica</i> <i>Punica granatum</i>	Lee et al. 2004; Chen et al. 1999; Zhang et al. 2001; El-Tounsy et al. 2001; El-Tounsy and Rawaldi 2002; Machado et al. 2001; Seennim et al. 2000

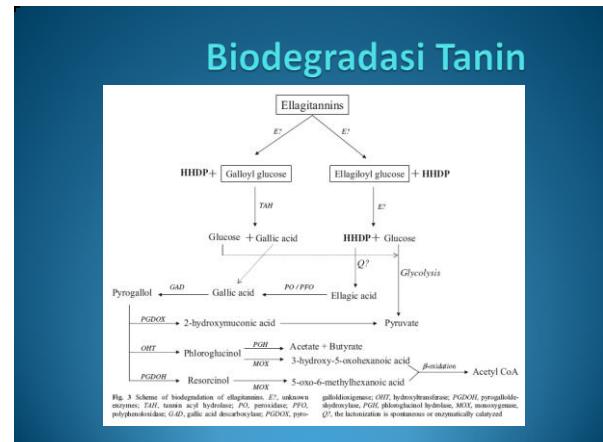
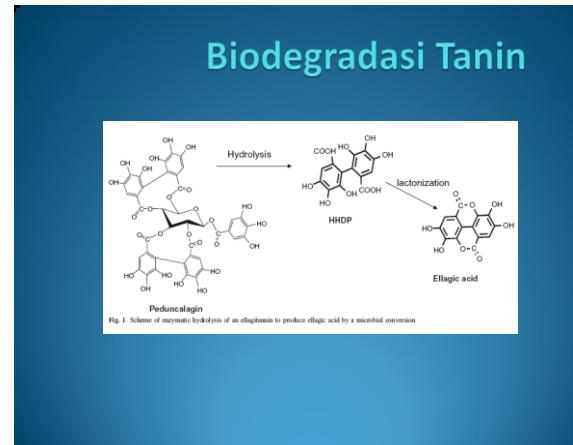
The key biosynthesis way is the 1,2,3,4,6-penta-O-galloyl-β-D-glucose formation.

**Table 2** Ellagitannins-rich plants of economical importance used as foods

Family	Latin name	Common name
Anacardiaceae	<i>Anacardium occidentale</i>	Cashew
	<i>Pistacia vera</i>	Pistachio nut
	<i>Mangifera indica</i>	Mango
Betulaceae	<i>Corylus avellana</i>	Hazelnut
Dioscoreaceae	<i>Dioscorea alata</i>	Potato
Fagaceae	<i>Castanea sativa</i>	Oaknut
Juglandaceae	<i>Juglans regia</i>	Nut
Myrtaceae	<i>Psidium guajava</i>	Guava tree
	<i>Eugenia caryophyllata</i>	Clove
	<i>Pimenta officinalis</i>	Green pepper
Punicaceae	<i>Punica granatum</i>	Pomegranate
Rosaceae	<i>Prunus domestica</i>	Plum
	<i>Prunus armeniaca</i>	Apricot
	<i>Prunus persica</i>	Peach
	<i>Prunus avium</i>	Wild cherry
	<i>Fragaria spp</i>	Strawberry
	<i>Rubus idaeus</i>	Raspberry
	<i>Rubus fruticosus</i>	Blackberry bush
	<i>Ribes nigrum</i>	Blackcurrant
	<i>Ribes grossularia</i>	Currant
Theaceae	<i>Camellia sinensis</i>	Tea
Vitaceae	<i>Vitis vinifera</i>	Grape
	<i>Vitis rotundifolia</i>	wine grape (moscato)

Source: Clifford and Sclafani (2000)

## Sumber Tanin



## Biodegradasi Tanin

Table 3 Microorganisms and ellagitannins-rich materials used for ellagic acid production

Microorganism	Culture system	Sources of Ellagitannins	References
<i>Lentinus edodes</i>	SSF	Cranberry pomace	Zhang and Shetty 2000, Vattem and Shetty 2003
<i>Rhizopus oligosporus</i>	SSF	Cranberry pomace	Vattem and Shetty 2002
<i>Aspergillus niger/Candida utilis</i>	Co-culture/Snf	Fruit shell of <i>Quercus aegilops</i> (valonea)	Shi et al. 2005
<i>Aspergillus SHL 6</i>	SnF	Fruit shell of <i>Quercus aegilops</i> (valonea)	Huang et al. 2005
<i>Aspergillus niger GH1</i>	SSF	Pomegranate husk	Robledo-Olivro et al. 2006, Aguilera-Cabio et al. 2007
<i>Aspergillus oryzae</i>	SnF	Acom fringe	Huang et al. 2007a
<i>Aspergillus oryzae/Trichoderma reesei</i>	SnF	Acom caps	Huang et al. 2007b, c
<i>Aspergillus niger PSH</i>	SSF	Leaves of creosote bush ( <i>Larrea tridentata</i> ) and tar bush ( <i>Fluorancia cornuta</i> )	Ventura et al. 2007
<i>Aspergillus niger GH1</i>	SSF	Leaves of creosote bush ( <i>Larrea tridentata</i> )	Aguilar et al. 2007a

## Farmakologi Tanin

Yang berperan dalam efek tanin terhadap sistem biologi adalah karena sifatnya :

1. Mengkelat ion logam
2. Presipitasi protein
3. Antioksidan biologis

### THERAPEUTIC VALUES OF TANNIN METABOLITES

- Mice consumed wine rich in phenolic components as catechin, epicatechin, gallic acid, ellagic acid showed increased antioxidant activity.
- Gallic acid (GA) also showed strong antioxidant activity by preventing lipid per-oxidation.
- GA is a strong antioxidant that possesses antimutagenic and anticarcinogenic activities  
**(Shahrzad et. al., 2001)**

- **Green tea contains:**

- (+)-**gallocatechin** (GC),
- (-)-**epicatechin** (EC),
- (-)-**epigallocatechin** (EGC),
- (-)-**epicatechingallate** (ECG),
- (-)-**epigallocatechingallate** (EGCG)

(c) Epigallocatechin gallate (EGCG), which shows numerous biological activities including antibacterial, antioxidant, anti-tumor and cancer preventive activities.

- Catechin serve as powerful antioxidant against lipid per oxidation when phospholipid bi-layers are exposed to aqueous oxygen radicals.

- (+)Catechin prevents cancer (liver, lung, breast and colon cancer) in at least one of three ways:

First, they can prevent the formation of carcinogens,

Second, they tone up the body's natural detoxification defenses, and

Finally, they suppress cancer promotion.

- (+)Catechin has other promising qualities:  
antibacterial and antiviral agent, regulating cholesterol and blood pressure, and reducing blood clotting tendencies that may cause heart attacks or strokes

## CONCLUSION

- Tannins & its monomers have profound effects on health.
  - Not advisable to take a large quantity of tannins, as they may be toxic.
  - It is important to determine the correct dosage of tannins for promoting optimal health.

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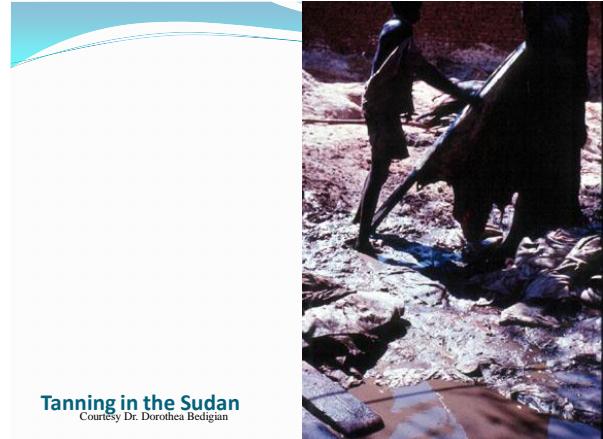
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## How tanning works

- Animal skins are made up of protein called collagen (among other things). This protein is readily degraded by bacteria and fungi.
  - When tannins bond to the collagen, the crosslinked fibers are no longer susceptible to attack.
  - The tannin must effectively crosslink the protein, but must also have desirable color properties and meet many other requirements.



## Tanning in the Sudan

Courtesy Dr. Dorothea Bedigian

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## **Tanning of hides**

- Hides are usually salted to prevent decomposition. The hides are first soaked in lime (or enzymes) to remove hair (depilatories).
  - The proper concentration of tannin solution must be used because if it is too concentrated, it seals the outside of the hide and the inside portions don't get tanned.

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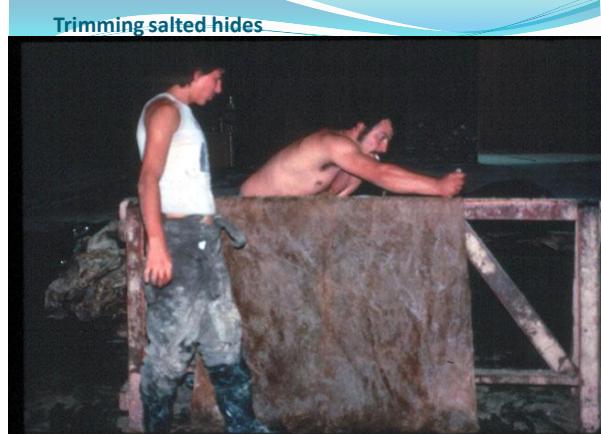
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Trimming salted hides



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Pickled hides

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Trimming pickled hides

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### Other uses of tannins

- Other uses of tannins account for about 15% of the total market.
- In the past, tannins and iron salts were used to make ink. Gums were also added.
- Tannins are sometimes used medicinally and are used in oil field drilling muds.