serum 12.3 g/100 ml was recommended). The buffer for gels contained 0.026 mole of H_3BO_3 and 0.014 mole of NaOH per litre, giving a final pH of 8.4 in the settled gel. The bridge solution contained 0.2 mole of H_3BO_3 and 0.04 mole of NaOH per litre. The potential gradient employed was 10 V/cm the positive electrode being in the upper vessel and the basic proteins migrating downwards to the cathode. All runs were made at 4°C. The cut gels were stained for 10 min. with Amido Black B and washed 4–5 times.

Results. The result obtained is shown in Fig. 2, in which 14 cathodic zones can be seen. On the anodic side there is one very diffuse region and one strongly stained band near the start which apparently corresponds to the least basic of the four bands in paper electrophoresis. At pH 7 all the protein material migrated towards the cathode. Thus the two anodic bands at pH 8.4 can also be considered to be basic proteins.

Under the conditions described here, the basic fraction of water-soluble barley grain proteins can be resolved reproducibly into 16 bands of significant intensity, which appear to be native components of barley grain.

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A Lignan Xyloside from the Sapwood of *Sorbus aucuparia* L.

V. P. ARYA, H. ERDTMAN, M. KROLIKOWSKA and T. NORIN

Institutionen för Organisk Kemi, Kungl. Tekniska Högskolan, Stockholm 70, Sweden

The isolation of two biphenyl derivatives of unusual structure, aucuparin and methoxyaucuparin from the heartwood of mountain ash (*Sorbus aucuparia* L.) has recently been reported from this laboratory.[1] The sapwood contains a lignan xyloside (1–3 % of the dry wood). This xyloside is identical with the lignan xyloside from *Alnus glutinosa* [2] and a *Lyonia* species [3] as shown by a comparison of the physical constants recorded in Table 1.

The investigation of the *Alnus* xyloside [4] showed that the aglycone has the ***structure*** I (X = H).

The *Sorbus* aglycone was obtained by the hydrolysis of the xyloside with acid as well as emulsin. This observation and the small difference in optical rotation between the xyloside and the aglycone indicates that the xyloside is a β-xyloside. Permanganate oxidation of the aglycone dimethyl ether in acetone afforded galloylgallic acid hexamethyl ether, m.p. 190–191°, and gallic acid trimethyl ether. Mild oxidation of the aglycone dimethyl ether with chromic anhydride in pyridine gave a lactone ("α-lactone"), $C_{18}H_{10}O_2(OCH_3)_6$, m.p. 200–201°, $[\alpha]_D$ −103° (a), −122° (c) and a cyclohemiacetal, $C_{18}H_{11}O(OH)(OCH_3)_6$, m.p. 180–181°, $[\alpha]_D$ −6° (c) [monoacetate, $C_{18}H_{11}O(OAc)(OCH_3)_6$, m.p. 158–160°, $[\alpha]_D$ −13° (c)] which on further oxidation furnished the α-lactone. The α-lactone gave the aglycone dimethyl ether on reduction with lithium aluminium hydride. On dehydration with potassium hydrogen sulphate the latter aglycone derivative afforded the anhydro-compound, $C_{18}H_{10}O(OCH_3)_6$, m.p. 145–146°, $[\alpha]_D$ −41.6° (a) as does the *Alnus* aglycone dimethyl ether.

The *Sorbus* xyloside dimethyl ether was oxidised with chromic anhydride in pyridine to an amorphous acid which on hydrolysis furnished the *Sorbus* "α-lactone". The sugar residue must be attached to the methylol group not suffering oxidation and the problem of elucidating the structure of the xyloside is therefore reduced to a determination of the structure of the α-lactone.

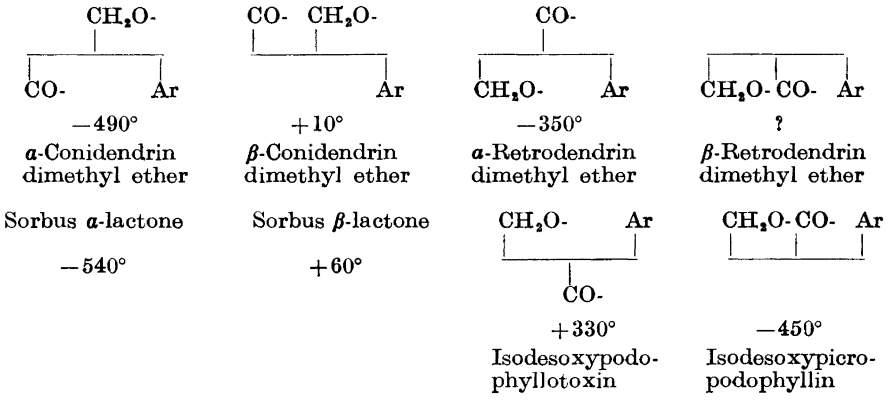
Table 1. (S,A and L = compounds from *Sorbus*, *Alnus* and *Lyonia*, respectively. $[\alpha]_D$ in acetone = a; in chloroform = c; in methanol = m).

Compound		Composition	M.P.	$[\alpha]_D$
Xyloside	S	$C_{18}H_{10}O(OCH_3)_4(OH)_3^{\alpha}(C_5H_{11}O_4)$	124–125°$^{\beta}$, 165–166°	+ 43° (m)
				+ 38° (a+aq)
	A		122–124°	+ 38° (a+aq)
	L		123°, 165°	+ 27° (a)
dimethyl ether	S	$C_{18}H_{10}O(OCH_3)_6(OH)^{\gamma}(C_5H_{11}O_4)$	143–145°	+ 45° (c)
hexaacetate	S	$C_{18}H_{10}O(OCH_3)_4(OAc)_3(C_5H_8O)(OAc)_2$	98–100°	− 1° (c)
hexabenzoate	S	$C_{18}H_{10}O(OCH_3)_4(OBz)_3(C_5H_8O)(OBz)_3$	138–139°	−2.5° (c)
Aglycone	S	$C_{18}H_{12}(OCH_3)_4(OH)_4^{\alpha}$	115–116°$^{\delta}$	+ 48° (a)
	A		165–167°$^{\delta,\varepsilon}$	+ 52° (a)
dimethyl ether	S	$C_{18}H_{12}(OCH_3)_6(OH)_2^{\gamma}$	163–164°	+ 45° (c)
				+ 32° (a)
	A		152°	- - - - -
	L		158–160°	+ 30° (a)
tetraacetate	S	$C_{18}H_{12}(OCH_3)_4(OAc)_4$	160–161	+ 21° (a), −11° (c)
	A		157–159°	+ 17° (a)
dimethyl ether diacetate	S	$C_{18}H_{12}(OCH_3)_6(OAc)_2$	99–100°	+ 29° (c)
	A		88– 89°	- - - - -

α: Of which two of the OH groups are phenolic. β: Sample containing two moles of water of crystallisation. γ: Alcoholic OH groups. δ: Probably dimorphism. ε: D,L-form [4], m.p. 115–118°.

This lactone could be isomerised with sodium ethoxide to a "β-lactone", $C_{18}H_{10}O_2(OCH_3)_6$, m.p. 152–153°, $[\alpha]_D$ + 13.8° (c), 0° (a), reduced by lithium aluminium hydride to a "β-diol", $C_{18}H_{12}(OCH_3)_6(OH)_2$, m.p. 171–172°, $[\alpha]_D$ +60.7° (c).

The large increase in optical rotation on epimerisation of the α-lactone recalls the similar effect observed on epimerisation of α-conidendrin dimethyl ether to the β-isomer with sodium ethoxide and suggests that the α-lactone might possess a structure and configuration similar to those of α-conidendrin dimethyl ether. However, a retrodendrin structure cannot be excluded since the specific rotation of α-retrodendrin dimethyl ether is similar in magnitude to that of α-conidendrin dimethyl ether and

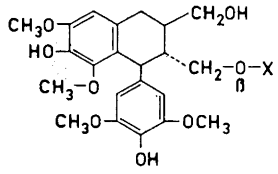


β-retrodendrin dimethyl ether is not known. For the following reason the latter should possess a high positive rotation. Isodesoxypodophyllotoxin and α-retrodendrin dimethyl ether are compounds of antipodal configuration and have rotations of similar magnitude but opposite sign. Similarly, isodesoxypicropodophyllin and β-retrodendrin dimethyl ether have antipodal configurations. Of these two compounds the former has a high negative rotation.

This is illustrated by the partial structures (see p. 519) in which the absolute configurations at C_2 (left), C_3 and C_4 (right) and the molecular rotations (in chloroform) of the relevant lignans are given. Like α-conidendrin dimethyl ether *Sorbus* α-lactone was not epimerised by heating with piperidine or sodium acetate. Under these conditions isodesoxypodophyllotoxin is epimerised to isodesoxypicropodophyllin.[5]

Additional confirmation of this conclusion can be obtained from a comparison of the molecular rotations in chloroform of some diols related to the *Sorbus* aglycone dimethyl ether given above.

The difference (+ 80°) in molecular rotations of the epimeric pair, α- and β-conidendryl alcohol dimethyl ether, is very similar to the difference (+ 72°) in molecular rotations of the *Sorbus* aglycone dimethyl ether and *Sorbus* "β-diol" and is also similar to that of the antipodal pair, isodesoxypodophyllyl alcohol and desoxypicropodophyllyl alcohol (−40°). It is concluded that *Sorbus* xyloside (= *Alnus* and *Lyonia* xyloside) has the structure and *configuration* I (X = xylose).



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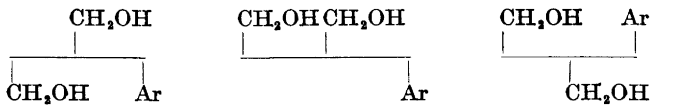
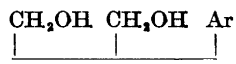


+ 80° α-Conidendryl alcohol dimethyl ether

+ 160° α-Conidendryl alcohol dimethyl ether

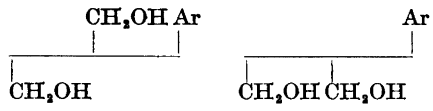
−90° Isodesoxypodophyllyl alcohol



+ 200° *Sorbus* aglycone dimethyl ether

+ 272° *Sorbus* "β-diol"

+ 480° Isodesoxypicropodophyllyl alcohol



−640° Desoxypodophyllyl alcohol

−130° Desoxypicropodophyllyl alcohol

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