

durch CN^- , das den für die Elution der Aminosäuren aus den Ionenaustauschersäulen benutzten Puffern zugesetzt wird. Die optimale Menge wurde durch eine Versuchsreihe zu 4 ml 0.01 M KCN-Lösung für 300 ml Puffer (entsprechend einer Pumpenfällung der automatischen Apparatur) ermittelt. In der Fig. 1 sind als Beispiel die Flächenwerte der für 1 μMol Lysin mit dem neuen Reagenz registrierten Kurven den entsprechenden Werten, die mit dem Reagenz nach MOORE UND STEIN¹ erhalten wurden, in Abhängigkeit von der Zeit, gegenübergestellt. Hierbei wurde die jeweilige Reagenzlösung während der angegebenen Zeitspanne unter Lichtabschluss bei Raumtemperatur, jedoch nicht unter Stickstoff aufbewahrt.

Die Figur zeigt die eindeutig bessere Lagerfähigkeit des neuen Reagenzes, die es ermöglicht, die Arbeiten an der automatischen Apparatur auch für mehrere Tage zu unterbrechen, ohne die Ninhydrinlösung ausfüllen zu müssen. Die beschriebene Methode lässt sich analog auch auf die Bestimmung von Aminosäuren in den durch Fraktionssammler gewonnenen Eluat anwenden.

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² H. STEGEMANN, *Z. physiol. Chem.*, 319 (1960) 102.

³ D. H. SPACKMAN, W. H. STEIN UND S. MOORE, *Anal. Chem.*, 30 (1958) 1190.

⁴ G. KRAMPITZ, *Z. Tierphysiol., Tierernähr.u. Futtermittelk.*, 15 (1960) 40.

⁵ K. HANNIG, *Clin. Chim. Acta*, 4 (1959) 51.

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The sorption of phenols from arabogalactan solutions (*Larix occidentalis* Nutt.) by anion exchangers

The anion exchange technique has been used for the recovery of phenols from phenolic wastes^{1,2} and for the sorption of phenolic aldehydes³. It has also been reported⁴ that strong anion exchangers in the hydrogen sulfite form can be used to separate guaiacyl phenols from catechol derivatives. Further studies⁵ showed that various phenols are sorbed on anion exchangers saturated with oxyanions of some elements of groups III-VI of the periodic table. Attempts have also been made to use anion exchange resins for the uptake of tan-colored compounds⁶, mainly phenolic⁷, from aqueous arabogalactan solutions from *Larix occidentalis* Nutt., the Western Larch. However, the polysaccharide was still light colored on precipitation with ethanol.

This note reports an exploratory investigation of the purification of arabogalactan solutions from Western Larch by means of anion exchangers in the free base (OH^-),

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chloride (Cl^-) or molybdate (MoO_4^{2-}) forms using water or methanol-water (1:2) as eluent.

When a 5 ml sample of a turbid, tan-colored and acidic (pH 4.3) arabogalactan solution was passed through a column of a weak anion exchanger (Amberlite IR-45 or Dowex-3) in its OH^- form or a strong anion exchanger (Amberlite IRA-400) in its Cl^- form, using water as eluent, the break-through order of some phenols was almost the same as that of arabogalactan. On the other hand, when the procedure was carried out with Amberlite IRA-400 in its OH^- form an almost 80 % loss of the arabogalactan resulted, owing to retention on the column.

Although it has been reported that the elution of phenols increases with increasing methanol concentration, an improved separation of arabogalactan and phenols was obtained with Amberlite IR-45 in its OH^- form when the eluent was methanol-water as, shown in Table I. The reason for this is not yet quite clear but it

TABLE I
SORPTION OF PHENOLS BY AMBERLITE IR-45 IN OH^- AND MoO_4^{2-} FORMS

Form	Eluenta	Break-through vol. (ml)		Recovery of A.G. % ^c
		A.G. ^b	Phenols	
OH^-	Water	25	25	—
OH^-	Methanol-water (1:2)	20	110	91.5 ^d
MoO_4^{2-}	Water	31	48	97.7 ^e
MoO_4^{2-}	Methanol-water (1:2)	30	225	99.4 ^d

^a Elution rate: 1 ml/min.

^b A.G. = arabogalactan.

^c Free from phenolic compounds.

^d Isolated by precipitation with ethanol.

^e Isolated by freeze-drying.

seems that the solubility relations could give an explanation. Most of the phenols identified earlier in different species of *Larix* genus^{8,9} (taxifolin, 3,3',4',5,7-pentahydroxyflavanone and aromadendrin, 3,4',5,7-tetrahydroxyflavanone, amongst others) and low molecular weight lignin material^{7,9} are primarily sparingly soluble in water, but are kept in suspension by the high solid dispersing power of the arabogalactan. When the methanol changes the solubility of the arabogalactan-phenolic system, the intermolecular forces, such as those involved in possible hydrogen bridges or some types of physical bonding, will be disrupted. Consequently, some chemisorption of these phenols on the resin should be taken into consideration in this case.

The mechanism for sorption of *o*-dihydroxyphenols by resin in its MoO_4^{2-} form has been related to true chelation⁵, *viz.* for taxifolin type constituents of the arabogalactan solution. The sorption of phenols of other configurations from an aqueous solution seems also to be increased as shown in Table I. It is also evident that the influence of methanol on the sorption efficiency is more apparent here than for the same resin in free base form.

The results of the sorption using this technique with Amberlite IR-45 in its OH⁻ or MoO₄²⁻ form with methanol-water as eluent can be summarized as follows: the colorless and phenol-free effluent, from which a white arabogalactan preparation can be isolated, was perfectly clear and neutral in contrast to the turbid, tan-colored, acidic and phenol-positive reacting crude arabogalactan solution. The $[\alpha]_D^{20}$ was + 12.00° compared with + 12.32° for a carbon-decolorized solution⁷. If the crude arabogalactan solution was pretreated with a cation exchanger (e.g. Amberlite IR-120) then the ash content of the isolated arabogalactan was lowered from 0.3 to < 0.02 %.

Experimental

The resins were purified in the usual way¹⁰ before packing a 10 × 350 mm column by the wet-packing method. The resins used were of chromatographic grade and saturation was performed by equilibration in 1 M solutions of the saturating compound. Before each experiment the resins were washed with the influent used for elution. The effluents were tested for phenols with the FOLIN-DENIS' reagent¹¹. The arabogalactan content of the preparation was approximately 97 %⁷; the preparation was dissolved in the solvent used, to give 3 % solutions.

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- ¹ R. E. ANDERSON AND R. D. HANSEN, *Ind. Eng. Chem.*, 47 (1955) 71.
- ² M. G. CHASANOV, R. KUNIN AND F. MCGARVEY, *Ind. Eng. Chem.*, 48 (1956) 305.
- ³ O. SAMUELSON AND F. GÄRTNER, *Acta Chem. Scand.*, 5 (1951) 596.
- ⁴ T. ENKVIST AND J. HALMEKOSKI, *Suomen Kemistilehti*, B 32 (1959) 173.
- ⁵ J. HALMEKOSKI, *Ann. Acad. Sci. Fennicae*, A II, 96 (1959).
- ⁶ H. BOUVENG AND B. LINDBERG, *Acta Chem. Scand.*, 12 (1958) 1977.
- ⁷ K. H. EKMAN, *Purification Studies on Crude Arabogalactan*, unpublished research, Washington State University, D. I. R. (1961).
- ⁸ J. GRIPENBERG, *Acta Chem. Scand.*, 6 (1952) 1153; G. V. NAIR AND E. VON RUDLOFF, *Can. J. Chem.*, 37 (1959) 1608; 38 (1960) 177.
- ⁹ H. V. BREVERTON, *New Zealand J. Sci. Technol.*, B37 (1956) 626.
- ¹⁰ O. SAMUELSON, *Ion Exchangers in Analytical Chemistry*, John Wiley & Sons, Inc., New York, 1953, p. 95.
- ¹¹ O. FOLIN AND W. DENIS, *J. Biol. Chem.*, 22 (1915) 305.

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