

none by the Clemmensen procedure was found to give the pinacolone, 1,2,2,2-tetra-*p*-fluoro-phenylethanone-1.

LAWRENCE, KANSAS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## Recovery of Sucrose from Cane Blackstrap and Beet Molasses

BY W. W. BINKLEY<sup>1</sup> AND M. L. WOLFROM

The crystallization of sucrose from the juices of the two main plant sources, the sugar cane and the sugar beet, constitutes a major industry. After all of the sucrose has been removed by crystallization procedures to the extent that is feasible, there remains a mother liquor which is known as molasses. That from the sugar cane, commonly known as blackstrap, is used mainly as a source of alcohol. Various attempts have been made to recover further amounts of sucrose from blackstrap molasses after prior removal of the reducing sugars with invertase-free yeasts (Olivarius process<sup>2</sup>), lime (Battelle process<sup>3</sup>) or barium hydroxide (Holven process<sup>4</sup>). None of these methods have proved commercially successful. The molasses from the sugar beet, however, is processed in various ways to recover further sucrose. The methods employed rest upon the separation of sucrose as a chemical derivative, generally a metallic saccharate, from which the sucrose is regenerated.

In the work herein recorded, we wish to report the application of chromatographic procedures to the recovery of sucrose from cane or beet molasses. To this end, the molasses was adsorbed on a native clay and the chromatogram was developed with dilute ethanol. From the effluent (Table I) the sucrose was readily crystallized as a colorless, high purity product. From the cane blackstrap molasses, there was recovered 74% of the sucrose present; from the beet molasses, the recovery was 93%. The nature of the effluent was further investigated by collecting it in the series of fractions shown in the table. Fractions 2, 3 and 4 (Table I) of the effluent from the cane molasses possessed a strong, pleasant and rum-like odor. The residual sirups from the sucrose crystallizations with the cane molasses were highly palatable.

The procedure employed in this work is an adaptation to the materials in hand of the general chromatographic procedures developed in this Laboratory<sup>5</sup> and especially those<sup>5b</sup> employing clay as an adsorbent. Further work is in progress to

determine the non-sucrose constituents of the fractions herein separated.

### Experimental

**Cane Blackstrap Molasses.**—The cane blackstrap molasses was produced in Cuba by the Cunagua Central of the American Sugar Refining Co., New York, N. Y.<sup>6</sup> It was stored at 8–10°. This molasses was obtained from a mixture of 75–80% Javan varieties POJ 2714 and POJ 2878 and 20–25% Cuban stock termed Crystalina.

*Anal.* (% original molasses) Solids, 82.3; ash, 5.5; sucrose,<sup>7</sup> 32; reducing sugars (as invert sugar),<sup>8</sup> 15; *d*, 1.468 g. per ml. at 25°; color, nearly black; taste, burnt sweet.

**Adsorption of Cane Blackstrap Molasses on Clay.**—An amount of 50 g. of the above cane blackstrap molasses was diluted with 25 ml. of distilled water. A smooth paste was prepared by the addition of 25 g. of a mixture of 5 parts (by wt.) of clay<sup>9</sup> and 1 part of "Celite"<sup>10</sup> to the diluted molasses. This paste was suspended, employing good agitation, in 500 ml. of absolute ethanol.

**Sucrose Separation from Cane Blackstrap Molasses.**—The molasses-clay-"Celite"-ethanol suspension was added at the top of a 7–9 by 11–12 cm. column<sup>11</sup> of a mixture (250 g.) of 5/1: clay/"Celite" in a 2-liter percolator arranged to permit the collection of the effluent without interfering with the operation of the column. The chromatogram was developed with three liters of 95% ethanol (the azeotrope). A total of 11.87 g. of sucrose (74.2% of that present) of excellent purity was obtained on concentration of the effluent. The residual sirup obtained on solvent removal was sweet and highly palatable. The nature of the effluent was investigated by collection in nine fractions, data on which are given in Table I. Fraction 2 was light green in color; fractions 3 to 8 were a golden color; fractions 8 and 9 were nearly colorless. Fractions 2, 3 and 4 had strong, pleasant, rum-like odors and it was obvious that the characteristic flavoring substances were concentrated therein. The other fractions had virtually no odor. The residual sirups obtained on solvent removal were sweet and highly palatable.

**Beet Molasses.**—The beet molasses was produced by the Michigan Sugar Co., Saginaw, Michigan.<sup>12</sup> It was stored at 8–10°.

*Anal.* (% original molasses) Solids, 81.2; ash, 2.0; sucrose,<sup>7</sup> 46.6; raffinose,<sup>7</sup> 2.2; reducing sugars, absent; *d*, 1.416 g. per ml. at 25°; color, brown.

**Adsorption of Beet Molasses on Clay.**—An amount of 50 g. of the above beet molasses was adsorbed on 30 g. of clay as described above for cane molasses.

**Sucrose Separation from Beet Molasses.**—The chromatogram was developed as described above for cane black-

(1) Sugar Research Foundation Associate of The Ohio State University Research Foundation (Project 190).

(2) H. DeF. Olivarius, U. S. Patents 1,730,473 (1929), 1,788,628 (1931).

(3) E. E. Battelle, U. S. Patents 1,044,003 (1913), 1,044,004 (1913).

(4) A. L. Holven, U. S. Patents 1,878,144 (1933), 1,878,145 (1933).

(5a) W. H. McNeely, W. W. Binkley and M. L. Wolfrom, *THIS JOURNAL*, **67**, 527 (1945); (b) B. W. Lew, M. L. Wolfrom and R. M. Goepf, Jr., *ibid.*, **67**, 1865 (1945); **68**, 1449 (1946); (c) L. W. Georges, R. S. Bower and M. L. Wolfrom, *ibid.*, **68**, 2169 (1946).

(6) We are indebted to Mr. Louis A. Wills of the above company for this material.

(7) Modified Clerget method.

(8) Munson-Walker method.

(9) Florex XXX, manufactured by the Floridin Co., Warren, Pennsylvania.

(10) No. 535, manufactured by Johns-Manville Co., New York, N. Y.

(11) Column dimensions refer to the adsorbent.

(12) We are indebted to Mr. Geoffrey S. Childs of the above company for this material.

TABLE I  
 EFFLUENT FRACTIONS FROM THE CHROMATOGRAM OF MOLLASSES ON CLAY

Type of molasses	Fraction	Volume of fraction, ml.	Solids in fraction, g.	Sucrose				
				First crop g.	M. p., °C.	$[\alpha]_D^{25}$ , c 5, water	Second crop g.	$[\alpha]_D^{25}$ , c 5, water
Cane blackstrap	1	450	0.3	...			..	
	2	260	.3	...			..	
	3	130	.6	...			..	
	4	290	5.9	2.74			0.11	
	5	310	6.7	2.91	180-182	+66.8°	.17	
	6	400	6.5	2.80			.16	
	7	370	3.7	1.00	179-181		.45	
	8	180	1.0	0.07			.37	
	9	1280	2.4	1.09	180-182		..	
	Total	3670	27.4	10.61	180-182 <sup>a</sup>	+65.9°	1.26	+65.0°
Beet	1	270	0.2	...			..	
	2	190	.2	0.05			..	
	3	200	.2	.15	180-182		0.05	
	4	210	1.4	.30			.44	
	5	230	2.8	1.44	180-182		.68	
	6	390	4.9	2.92	180-182	+66.7°	.90	
	7	470	5.5	2.70	180-182		2.46	
	8	360	5.3	1.89			1.87	
	9	350	3.9	1.00	180-182		1.97	
	10	350	2.6	1.70			..	
	11	880	1.9	1.21	180-182		..	
	Total	3900	28.9	13.36	180-182 <sup>a</sup>	+66.5°	8.37	+64.0°

<sup>a</sup> Mixed melting point with sucrose (m. p. 180-182°) of composite samples: from cane blackstrap molasses, 180-182°; from beet molasses, 180-182°.

strap molasses. The effluent was collected in eleven fractions. Data on these fractions are listed in Table I. Fractions two and three of Table I had a strong, unpleasant odor characteristic of beet molasses; all of the fractions were nearly colorless. A total of 21.7 g. of sucrose (93.3% of that present) of excellent purity was obtained on concentration of the effluent. The residual sirups obtained on complete solvent removal were unpalatable.

**Acknowledgment.**—We are pleased to acknowledge the assistance in this work of Mr. John Kolbas.

### Summary

When either cane blackstrap molasses or beet molasses is adsorbed on a suitable clay and the chromatogram so obtained is developed with dilute alcohol, a high purity, crystalline sucrose is recoverable from the effluents in a yield of 74% of the sucrose present for cane blackstrap molasses and 93% for beet molasses.

COLUMBUS, OHIO

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## A Diffusion Study of Lignin Sulfonic Acids in Sulfite Waste Liquor

BY DERROL PENNINGTON AND D. M. RITTER

Available data support the conclusion that lignin sulfonic acids from the sulfite wood pulping process not only exhibit chemical inhomogeneity but are heterogeneous in respect to their molecular weights, which are thought to be high. Unfortunately, however, most values given in the literature offer only qualitative evidence of the molecular size. Their variations from 400 to 6,000 suggest the cryoscopic method by which they were determined to be unsuitable for use with lignin sulfonic acids.<sup>1</sup> This is not surprising

(1) P. Klason, "Beitrag zur chemischen Zusammensetzung Fichtenzholzes," Berlin, 1911, pp. 18, 37; *Arkiv. Kemi Mineral. Geol.*, **6**, 13

since cryoscopic data are expressive of thermodynamic activities and their interpretation in terms of the molecular dimensions for polyvalent strong electrolytes such as lignin sulfonic acids is complicated by lack of knowledge of activity coefficients and degrees of dissociation. Interpretation of osmotic pressure data is subject to the same difficulties and is further complicated by the inevitable presence of Donnan equilibria. Reproducible molecular weights of 400 to 20,000

(1917); *Chem. Zentr.*, **90**, I, 62 (1919); K. Melander, *Kemi Och Bergvetenskap*, 10-12 (1918); *Medd. fra Pappersmk.*, **29**, 1921; M. Samec and I. Ribaric, *Kolloidchem. Beihefte*, **24**, 157 (1927).