

Reaction of Furfuryl Alcohol, Furfuryl Methyl Ether and 2,5-Dimethoxy-2,5-dihydrosilvan with Methanolic Hydrogen Chloride

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The products formed by interaction of methanolic hydrogen chloride and furfuryl alcohol, furfuryl methyl ether and 2,5-dimethoxy-2,5-dihydrosilvan, respectively, have been analyzed by fractional distillation. Four new compounds, *viz.* 2,3 (or 4), 5-trimethoxytetrahydrosilvan, methyl levulinate dimethyl ketal, α (or β)-methoxylevulinaldehyde dimethyl acetal and 1,1,2 (or 3), 4,4-pentamethoxypentane were identified and at least three unknown compounds were shown to be present. Earlier experiments in this field, in particular by Pummerer *et al.*, *Ber.* 56 (1923) 999; 68 (1935) 480, are discussed.

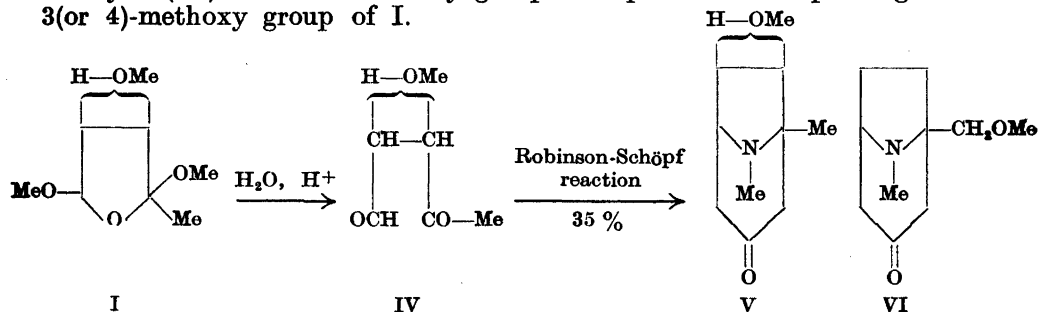
By heating furfuryl alcohol, furfuryl methyl ether and 2,5-dimethoxy-2,5-dihydrosilvan, respectively, under reflux with methanolic hydrogen chloride, distillable mixtures of liquid compounds were obtained and separated by fractional distillation under 21 mm through a 25 cm column (distillation time 8—10 days). The results of the distillations are shown in Fig. 1. The fractions were mainly identified by measuring the refractive index and the infrared absorption, and by analyses. Three new compounds, *viz.* 2,3 (or 4), 5-trimethoxytetrahydrosilvan (I), methyl levulinate dimethyl ketal (II) and α (or β)-methoxylevulinaldehyde dimethyl acetal (III) were identified, and at least 3 unknown compounds were shown to be present. The yields of the various compounds are given in Table 1.

I is stable towards alkali and shows no absorption band around 5.8 μ . Hydrolysis with 0.025 *N* hydrochloric acid gives a reaction product, which condenses with methylamine and acetonedicarboxylic acid (Robinson-Schöpf reaction) to a tropinone $C_9H_{14}ON(OMe)$, which is different from the known 1-methoxymethyltropinone (VI) and therefore is 1-methyl-6(or 7)-methoxytropinone (V). From this, and from the fact that I not only is formed from furfuryl alcohol and furfuryl methyl ether, but also from dimethoxydihydrosilvan, it is inferred that the compound is either a 2,3,5- or a 2,4,5-trimethoxy-

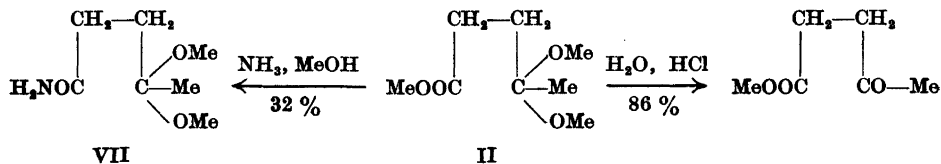
Table 1. Yields of compounds present in the reaction mixtures prepared from furfuryl alcohol, furfuryl methyl ether and dimethoxydihydrosilvan.

Compound	Yield, % based upon			Yield, % of distillable product from		
	Furfuryl alcohol	Furfuryl methyl ether	Dimethoxydihydrosilvan	Furfuryl alcohol	Furfuryl methyl ether	Dimethoxydihydrosilvan
I. [2,3 (or 4), 5-Tri-methoxytetrahydrosilvan]	3.0	1.8	2.8	7	5	4
Methyl levulinate	27.7	11.2	15.2	65	32	22
II. (Methyl levulinate dimethyl ketal)	1.2	15.3	33.8	3	44	49
III. [α (or β)-Methoxy-levulin-aldehyde dimethyl acetal]	10.1	0.0	0.0	24	0	0
Unknown compounds	0.3	6.2	17.3	1	18	25
Total yield of distillable compounds	42.3	34.5	69.1	100	100	100

tetrahydrosilvan and that the product of hydrolysis is α - or β -methoxylevulin-aldehyde (IV) with the methoxy group in a position corresponding to the 3(or 4)-methoxy group of I.



II is transformed into methyl levulinate by heating under reflux with methanolic hydrogen chloride containing 1.07 mole of water. Reaction with ammonia gives a crystalline compound with the formula $C_5H_9ON(OMe)_2$. From this it is inferred that II is methyl levulinate dimethyl ketal and that the nitrogen containing compound is the corresponding amide (VII).



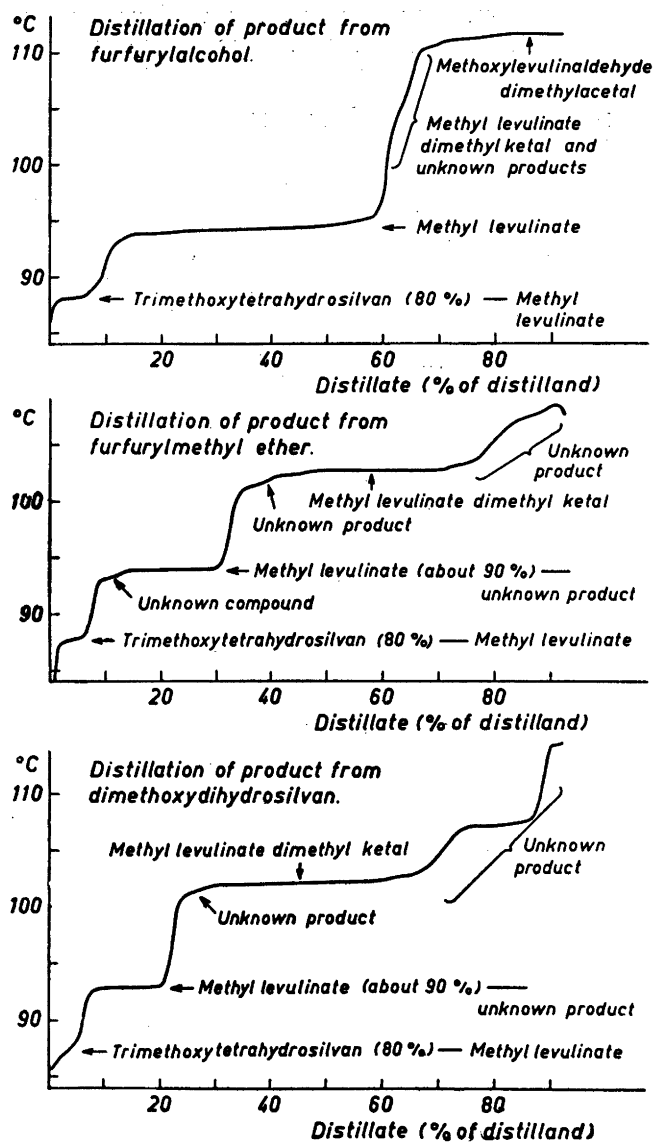
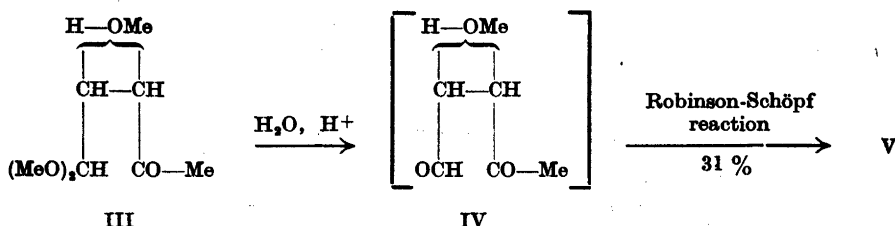


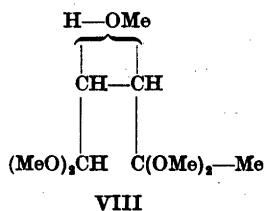
Fig. 1. Curves for the distillations of the reaction mixtures prepared from furfuryl alcohol, furfuryl methyl ether and dimethoxydihydrosilvan.

III is unstable towards alkali. Hydrolysis with hydrochloric acid and condensation of the reaction product with methylamine and acetonedicarboxylic acid give a tropinone, which is identical with V. From this it is inferred that the product of hydrolysis is either α - or β -methoxylevulinalehyde (IV)

and that III is α - or β -methoxyacetaldehyde dimethyl acetal with the methoxy group in a position corresponding to the position of the 3(or 4)-methoxy group of I.



The percentage of unknown compounds in the distillate from furfuryl alcohol is small compared to the percentage in the distillates from furfuryl methyl ether and dimethoxydihydrosilvan, respectively. As about 4 % (by weight) of methanol is slowly split off during the distillation of the reaction products from furfuryl methyl ether and dimethoxydihydrosilvan we assumed that a number of the unknown compounds are formed from 1,1,2(or 3),4,4-pentamethoxypentane (VIII) by loss of one or two moles of methanol.



In order to test this hypothesis, the reaction mixture from furfuryl methyl ether was heated under reflux with a solution of potassium hydroxide in methanol. This should remove all esters and all compounds containing free carbonyl groups. The resulting product was then distilled rapidly under 12 mm through a 12 cm column (distillation time 12 hours). The result of the distillation is shown in Fig. 2 and the yields of the products, based upon furfuryl methyl ether, are given in Table 2.

VIII is stable towards alkali and shows no absorption band around 5.8μ . Acid hydrolysis followed by a Robinson-Schöpf reaction gives the tropinone V.

Table 2. Yields of alkali-resistant compounds from furfuryl methyl ether.

Compound	Yield, % based upon furfuryl methyl ether
2,3 (or 4)-Trimethoxytetrahydrosilvan (I)	1.1
Unknown compounds	about 2.5
1,1,2 (or 3), 4,4-Pentamethoxypentane (VIII)	0.7

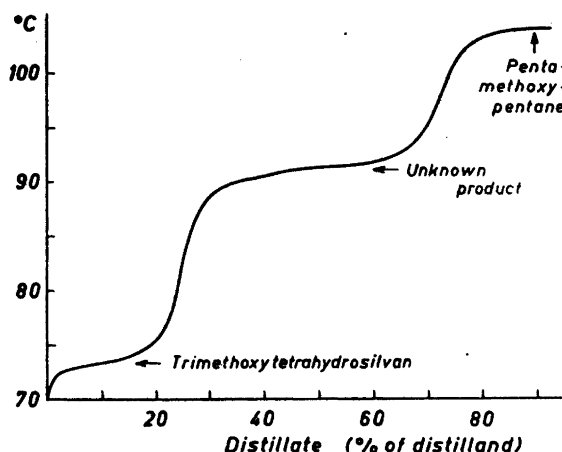


Fig. 2. Curve for the distillation of alkali-treated reaction product from furfuryl methyl ether.

From this it is inferred that the product of hydrolysis is α - or β -methoxylevulin-aldehyde (IV) and that VIII is 1,1,2 (or 3),4,4-pentamethoxypentane with the 2(or 3)-methoxy group in a position corresponding to the position of the 3(or 4)-methoxy group of I.

Although the pentamethoxypentane VIII has thus been isolated, the yield is much lower than the yields of unknown compounds from the distillations of the reaction mixtures from furfuryl methyl ether and dimethoxydihydrosilvan. However, we still think that VIII is the progenitor of the major portion of the unknown compounds and that the yield of VIII in the isolation experiment is low, because most of the compound has been hydrolyzed or transformed in other ways during the alkaline treatment and the isolation.

The formation of acetals of α (or β)-methoxylevulin-aldehyde (IV) in the reaction of dimethoxydihydrosilvan with methanolic hydrogen chloride is just another example of the known addition of an alcohol to the 3,4-double bond of 2,5-dimethoxy-2,5-dihydrofurans by the action of the alcohol and a catalytic amount of a strong acid¹. The formation of derivatives of IV from furfuryl alcohol and furfuryl methyl ether may, on the other hand, be taken as proof of the initial formation of dimethoxydihydrosilvan or its equivalent during the fission of furfuryl alcohol and furfuryl methyl ether, respectively. This is consistent with experiments with similar compounds as well as with theoretical considerations^{2, 3, 4}.

The distillable reaction product from furfuryl methyl ether has by and large the same composition as the product from dimethoxydihydrosilvan. The composition of the product from furfuryl alcohol is somewhat different, but this becomes understandable if one takes into account that in any reaction between furfuryl alcohol and methanol there is an excess of one mole of water over similar reactions with furfuryl methyl ether and dimethoxydihydrosilvan, respectively.

In spite of the similarity in composition, the yield of distillable product from dimethoxydihydrosilvan is almost twice as large as from furfuryl alcohol and furfuryl methyl ether, respectively. This can be understood by assuming that the fission reactions of furfuryl alcohol and furfuryl methyl ether to distillable products compete with other reactions leading to non-distillable products (polymerisation reactions), while the reactions of all the compounds roughly speaking follow the same path after the furans have been rearranged to dimethoxydihydrosilvan or its equivalent.

Pummerer *et al.*^{5,6} (*cf.* also ⁷) have previously investigated the action of methanolic hydrogen chloride on furfuryl alcohol and furfuryl methyl ether and the reaction conditions given by these authors have been followed here. From the reaction product from furfuryl alcohol they isolated 2 % of impure methyl levulinate and 19 % of a product, which, judging from their experimental data, was a mixture of two or more compounds, but which was claimed to be 5-methoxylevulinaldehyde dimethyl acetal.

The correctness of the experimental data of Pummerer *et al.*, as well as the deductions based thereon, have previously been questioned^{2,3}. The experiments presented here are on the whole consistent with the main findings of Pummerer *et al.* (*cf.* also ⁷), but their claim to have identified 5-methoxylevulinaldehyde, as well as all deductions based on this claim⁵⁻⁸, cannot be accepted.

EXPERIMENTAL

Microanalyses by Ernst Boss and Kirsten Glens

Reaction of furfuryl alcohol with methanolic hydrogen chloride (*cf.*^{2,3}). Furfuryl alcohol (161 g, 1.64 mole), methanol (dried with magnesium, 1840 ml) and acetyl chloride (17.0 ml) were mixed and heated under reflux (3 h)⁶. After cooling a solution of sodium methoxide [from sodium (5.70 g) and methanol (70 ml)] was added and the mixture brought to pH 7 (test with wet indicator paper) by addition of small amounts of glacial acetic acid or sodium methoxide. The methanol was evaporated in a vacuum from a water-bath, a precipitate removed by filtration and washed with ether, and the filtrate distilled. The yield was 110.8 g of a slightly yellow liquid (b.p.₀, 43–75°).

110.3 g of this product was fractionally distilled through a 25 cm packed column⁸ into 26 fractions of approximately the same size (distillation pressure 21 mm, heat input 3.7 watt, take-off every 6.9 minutes, change of fraction every 8 hours, total distillation time 9 days) (Fig. 1). The refractive index and the infrared absorption of all fractions were measured. The yield of distillate was 102.7 g (93 % of distilland).

(a) *The distillate boiling at about 88°* (n_D^{25} 1.4235) (2.48 g) was heated under reflux (40 min) with sodium hydroxide (8 %, 10 ml) and the reaction mixture continuously extracted with ether. Distillation of the ethereal extract gave 1.61 g of 2,3(or 4),5-trimethoxytetrahydrosilvan (I) (colorless liquid, b. p.₁₀ 75°, n_D^{25} 1.4239). The compound showed no absorption band around 5.8 μ . (Found: C 54.7; H 9.1; OCH₃ 51.6. Calc. for C₅H₇O(OCH₃)₃ (176.2): C 54.5; H 9.2; OCH₃ 52.8).

I (0.700 g, 0.0040 mole) was heated under reflux (10 min) with 0.025 *N* hydrochloric acid (4.0 ml). After cooling, the light-yellow reaction mixture was added to a solution of acetonedicarboxylic acid (1.80 g), methylamine hydrochloride (0.84 g), citric acid (3.00 g) and sodium hydroxide (2.36 g) in water (68 ml). The resulting solution (pH 5.0) was left standing (48 h) at room temperature. Potassium carbonate (anhydrous, 35 g) was added and dissolved, and the solution continuously extracted with ether. The ether was removed from the ethereal extract by distillation. The oily residue was dissolved in ethanol (5 ml) and added to a solution of picric acid (1.20 g) in hot ethanol (10 ml). Hereby 0.570 g (35 %) of methylmethoxytropinone picrate was obtained [m. p. 129–131° (Hershberg

apparatus, corr.]. Crystallization from ethanol gave 0.374 g (m. p. 135–136°; further crystallization did not change the m. p.). (Found: C 46.8; H 5.0; N 13.1; OCH₃ 6.6. Calc. for C₁₅H₁₇O₃N₄ (OCH₃) (412.4): C 46.6; H 4.9; N 13.6; OCH₃ 7.5).

The picrate was further characterized by its infrared spectrum (in potassium bromide), which was found to be different from the spectrum of 1-methoxymethyltropinone picrate (m. p. 164–170°), prepared from 2,5-dimethoxytetrahydrofurfuryl methyl ether¹⁰.

The aqueous layer from the ethereal extraction of trimethoxytetrahydrofurfurylvan was acidified to Congo red with concentrated hydrochloric acid and extracted further with ether. The ether was removed by distillation and the oily residue dissolved in water (5 ml). Semicarbazide hydrochloride (0.5 g) and sodium acetate (0.75 g) were added and dissolved. After standing for 30 minutes a precipitate of levulinic acid semicarbazone was removed by filtration. The yield was 361 mg [m. p. 187° (dec.) (Hershberg apparatus, corr.)]. Crystallization from ethanol gave 296 mg [m. p. 187° (dec.)]. (Found: C 41.5; H 6.3; N 24.6. Calc. for C₆H₁₁O₃N₃ (173.2): C 41.6; H 6.4; N 24.3).

From the above data, analyses and infrared spectra, it is inferred that the distillate boiling at 88° is an azeotrope of 80 % of trimethoxytetrahydrofurfurylvan and 20 % of methyl levulinate. In the separation experiment the yield of trimethoxytetrahydrofurfurylvan (1.61 g) thus corresponds to 81 % and of levulinic acid semicarbazone (361 mg) to 55 %. (Found: C 55.1; H 8.8; OCH₃ 47.5. Calc. for 80 % C₅H₇O(OCH₃)₃ + 20 % C₅H₇O₂ (OCH₃): C 54.7; H 8.9; OCH₃ 47.0).

From the distillation curve (Fig. 1) the yield of trimethoxytetrahydrofurfurylvan is estimated to 8.6 g (3.0 % based upon furfuryl alcohol) and of methyl levulinate to 2.2 g.

(b). The distillate boiling at about 94° (n_D^{25} 1.4201, n_D^{20} 1.4223, d_4^{20} 1.0490) is methyl levulinate, which previously has been prepared pure by Langlois and Wolff¹¹ (b. p.₁₅ 89–91°, n_D^{20} 1.4225, d_4^{20} 1.0495). (Found: C 55.4; H 7.9; OCH₃ 24.0. Calc. for C₅H₇O₂ (OCH₃) (130.1): C 55.4; H 7.8; OCH₃ 23.8).

The yield of methyl levulinate is 57.0 g. This brings the total yield of methyl levulinate up to 59.2 g (27.7 %).

(c). The distillate boiling at about 112° (n_D^{25} 1.4229) is α (or β)-methoxylevulinialdehyde dimethyl acetal (III) [yield 29.2 g (10.1 %)]. (Found: C 54.8; H 9.2; OCH₃ 52.6. Calc. for C₈H₇O(OCH₃)₂ (176.2): C 54.5; H 9.2; OCH₃ 52.8).

III (2.56 g) was shaken (20 h) with a solution of sodium hydroxide (8 %, 50 ml) and the reaction mixture continuously extracted with ether and distilled under 11 mm. The distilland was dark-red and only 0.3 g of distillate, b. p. 115–162°, could be collected. III is thus transformed into undistillable material under the influence of alkali.

III (0.700 g, 0.040 mole) was hydrolyzed and the hydrolysate treated with acetone-dicarboxylic acid and methylamine as described above. The yield of methylmethoxytropinone picrate was 0.504 g (31 %) (m. p. 135–136°). (Found: C 46.5; H 4.6; N 13.5; OCH₃ 6.6).

The infrared spectrum was identical with that of the picrate of the tropinone from trimethoxytetrahydrofurfurylvan.

(d). The distillate boiling between 94° and 112° contains

(1) a product (yield about 0.5 g), which has a larger refractive index than either methyl levulinate or methoxylevulinialdehyde dimethyl acetal. Of the fractions collected by us, the largest index (1.4258) was shown by the fraction (3.88 g) boiling from 103.1° to 108.2°. The product was not identified.

(2) Methyl levulinate dimethyl ketal [yield about 3.6 g (1.2 %)], which was identified by its spectrum. The fraction boiling from 103.1° to 108.2° was richest on ketal.

(3) A compound which turns yellow on standing. The compound, which is present in the fractions boiling above 103°, and in particular in the fraction boiling from 103.1° to 108.2°, was not identified. The yield of the compound is about 0.3 g. This brings the total yield of unknown compounds up to 0.8 g. Assuming an average molecular weight of 175, this corresponds to 0.3 %.

The yield of all distillable products from furfuryl alcohol is thus 42.3 %.

Reaction of furfuryl methyl ether with methanolic hydrogen chloride. Furfuryl methyl ether (184.0 g, 1.64 mole) was treated as described for furfuryl alcohol. The yield of distillable product was 101.9 g (b. p.₁₅ 57–79°), 100.9 g of which was fractionated (Fig. 1) into 24 fractions. During the later half of the distillation methanol was conti-

nously split off from the distilland. This was indicated by the accumulation of methanol in the cooling trap (3.8 g in all, n_D^{25} 1.3327). The yield of distillate, including the methanol, was 96.7 g (96 % of distilland).

(a). The distillate boiling at about 88° is identical with the 88°-distillate from furfuryl alcohol (inferred from the spectrum). The yield of trimethoxytetrahydrosilvan is 5.2 g (1.8 % based upon furfuryl methyl ether) and of methyl levulinate 1.3 g.

(b). The distillate boiling at about 94° (n_D^{25} 1.4218) is, as inferred from the spectrum and from analyses, an azeotrope of about 90 % of methyl levulinate and about 10 % of an unknown product, which has a considerably higher refractive index and a high content of methoxy groups. The yield of methyl levulinate is about 22.5 g and of the unknown product about 2.5 g. This brings the total yield of methyl levulinate up to 23.8 g (11.2 %). (Found: C 56.2; H 8.2; OCH₃ 26.2).

(c). The distillate boiling between 88° and 94° and in particular the fraction (4.35 g) boiling from 89.8° to 93.2°, turns yellow on standing. The compound responsible for the coloration was not identified (yield about 0.5 g), but is probably identical with the above mentioned compound from furfuryl alcohol having the same property.

(d). The distillate boiling at about 103° (n_D^{25} 1.4239) is methyl levulinate dimethyl ketal (II) [yield about 44.3 g (15.3 %)]. The compound showed no absorption band around 5.8 μ . (Found: C 54.9; H 9.4; OCH₃ 51.6. Calc. for C₈H₁₄O(OCH₃)₂ (176.2): C 54.5; H 9.2; OCH₃ 52.8).

II (3.00 g) was heated under reflux (3 h) with methanol (dried with magnesium, 3.0 ml) to which had been added water (310 mg) and concentrated hydrochloric acid (50 mg). Sodium (12 mg) was added and the mixture distilled. Hereby 1.90 g (86 %) of almost pure methyl levulinate was obtained (b. p.₁₃ 83–86°, n_D^{25} 1.4208). (Found: C 55.6; H 8.6; OCH₃ 25.5. Calc. for C₇H₁₂O₂(OCH₃) (130.1): C 55.4; H 7.8; OCH₃ 23.8).

II (3.80 g) was dissolved in a solution of methanol (10.0 ml), water (0.50 ml) and ammonia (2.3 g) and the resulting light-yellow solution left standing for 3 days. The solution was evaporated in a vacuum from a water-bath and the oily residue crystallized from benzene-petroleum ether. The resulting light-brown crystals were washed twice with benzene-petroleum ether and dried under 0.1 mm over sulfuric acid (3 h). The yield of impure levulinamide dimethyl ketal (VII) was 1.41 g (41 %) (m. p. 64–68°). Recrystallization from benzene-petroleum ether gave 1.10 g (32 %) of pure VII (slightly yellow crystals, m. p. 67–70°; further crystallization did not change the m. p.). (Found: C 52.1; H 9.5; N 9.1; OCH₃ 38.0. Calc. for C₇H₁₂ON(OCH₃)₂ (161.2): C 52.2; H 9.4; N 8.7; OCH₃ 38.5).

As explained in the following, only the intermediate fractions of the distillate boiling at about 103° are pure methyl levulinate ketal, while the first and the last fractions are contaminated with other compounds.

(e). The distillate boiling between 94° and 103° contains a product (yield about 1.4 g), which has a larger refractive index than either the 94°-azeotrope or methyl levulinate dimethyl ketal. Of the fractions collected by us, the largest index (1.4289) was shown by the fraction (3.88 g) boiling from 98.2° to 101.3°. The product which contaminates the first fractions of methyl levulinate dimethyl ketal was not identified, but is possibly identical with the above mentioned product from furfuryl alcohol having the same property.

(f). The distillate boiling above 103°. In this range at least one compound, which was not identified, was shown to be present as judged by the spectra. The compound contaminates the later fractions of the ketal. The data for the last 8 fractions of the distillation are given in Table 3.

The yield of unknown compounds boiling above 103° is about 15.0 g. This brings the total yield of unknown compounds up to 19.4 g. Assuming an average molecular weight of 190, this corresponds to 6.2 %.

The yield of all distillable compounds from furfuryl methyl ether is thus 34.5 %.

Reaction of dimethoxydihydrosilvan with methanolic hydrogen chloride. Dimethoxydihydrosilvan (237.0 g, 1.64 mole) was treated as described for furfuryl alcohol. The yield of distillable product was 209.0 g (b. p._{0.5} 53–74°), 121.8 g of which was fractionated into 32 fractions (Fig. 1). Methanol was split off from the distilland as in the furfuryl methyl

Table 3. Data for the last 8 fractions of the distillation of the reaction product from furfuryl methyl ether.

Fraction (g)	B. p. °C	n_D^{25}	C	H	OCH ₃
17 (3.69)	103.7	1.4239			
18 (3.73)	103.7—103.8	1.4239	55.7	9.4	51.1
19 (3.56)	103.8—104.2	1.4241			
20 (3.74)	104.2—104.8	1.4252	55.6	9.3	53.4
21 (3.92)	104.8—107.2	1.4278	55.6	9.3	56.7
22 (3.65)	107.2—108.4	1.4301	56.4	9.3	57.3
23 (3.80)	108.4—109.0	1.4291			56.4
24 (3.97)	109.0—109.8	1.4267			

ether experiment (yield 3.5 g, n_D^{25} 1.3397). The yield of distillate, including the methanol, was 115.4 g (95 % of distilland).

(a). The distillate boiling at about 87° is identical with the 88°-distillate from furfuryl alcohol. The yield of trimethoxytetrahydrosilvan is 4.7 g (2.8 % based upon dimethoxydihydrosilvan) and of methyl levulinate 1.2 g.

(b). The distillate boiling at about 93° (n_D^{25} 1.4212) is identical with the 94°-distillate from furfuryl methyl ether. The yield of methyl levulinate is about 17.7 g and of the unknown product about 2.0 g. This brings the total yield of methyl levulinate up to 18.9 g (15.2 %). (Found: C 55.7; H 8.1; OCH₃ 26.3).

(c). The distillate boiling at about 102° (n_D^{25} 1.4229) is methyl levulinate dimethyl ketal. The yield is about 56.9 g (33.8 %). (Found: C 54.5; H 9.4; OCH₃ 52.6).

(d). The distillate boiling between 93° and 102° contains a product (yield about 1.2 g), which has a larger refractive index than either the 93°-azeotrope or methyl levulinate dimethyl ketal. Of the fractions collected by us, the largest index (1.4249) was shown by the fraction (4.1 g) boiling from 101.0° to 101.6°. The product, which contaminates the first fractions of methyl levulinate dimethyl ketal, was not identified, but is possibly identical with the above mentioned product from furfuryl alcohol and furfuryl methyl ether having the same property.

(e). The distillate boiling above 102°. In this range at least 2 different compounds, which were not identified, were shown to be present as judged by the spectra. The lowest boiling of these, which is identical with the unknown compound boiling in the same range in the furfuryl methyl ether experiment, contaminates the later fractions of methyl levulinate dimethyl ketal. The data for the last 12 fractions of the distillation are given in Table 4.

The yield of unknown compounds boiling above 102° is about 28.0 g. This brings the total yield of unknown compounds up to 31.2 g. Assuming an average molecular weight of 190, this corresponds to 17.3 %.

The yield of all distillable products from dimethoxydihydrosilvan is thus 69.1 %.

Treatment of the reaction mixture from furfuryl methyl ether with methanolic potassium hydroxide. Furfuryl methyl ether (350.0 g) was heated under reflux with methanolic hydrogen chloride as described above. Potassium hydroxide pellets (250 g) were added and the mixture heated further under reflux (18 h). The major part of the methanol was removed from the black reaction mixture by distillation in a vacuum. Water (150 ml) was added and the remainder of the methanol was removed by distillation under 200 mm through a Vigreux type column. Another 150 ml of water was added and the mixture

Table 4. Data for the last 12 fractions of the distillation of the reaction product from dimethoxydihydrosilvan.

Fraction (g)	B. p. °C	n_D^{25}	C	H	OCH ₃
21 (4.13)	102.2–102.3	1.4230			
22 (4.11)	102.3–102.7	1.4232	55.7	9.7	52.8
23 (4.11)	102.7–102.9	1.4238			52.8
24 (4.08)	102.9–104.0	1.4250			54.1
25 (4.07)	104.0–106.2	1.4280			57.1
26 (4.08)	106.2–107.2	1.4296			58.0
27 (4.07)	107.2	1.4292			57.0
28 (4.07)	107.2–107.5	1.4286	55.1	9.4	57.2
29 (4.06)	107.5–107.8	1.4272			56.1
30 (3.97)	107.8–112.1	1.4286			56.4
31 (3.09)	112.1–114.8	1.4400			57.8
32 (0.41)	114.8–116.1	1.4485	56.1	9.3	54.6

continuously extracted with ether in a Kutscher-Steudel apparatus for 2 days. The black liquid in the boiling flask (2 layers) was shaken with anhydrous magnesium sulfate (100 g), filtered, and the magnesium sulfate washed with ether. The combined ethereal solutions (0.5 l) were shaken with a saturated solution of calcium chloride (0.5 l), dried with potassium carbonate and distilled under 0.2 mm. The yield of distillate was 25.3 g (colorless liquid, b. p. 65–71°, n_D^{25} 1.4254), a portion of which (23.2 g) was fractionated through a 12 cm column into 12 fractions (distillation pressure 12 mm, heat input 3.6 watt, take-off every 2.4 minutes, change of fraction every hour, total distillation time 12 hours) (Fig. 2 and Table 5). The infrared absorption of all fractions was measured. The yield of distillate was 21.5 g (93 % of distilland).

(a). The distillate boiling at about 73° is the same trimethoxytetrahydrosilvan as isolated above (inferred from the spectrum).

(b). The distillate boiling at about 91° consists of a main product (inferred from the spectrum) and another product, which turns yellow on standing. Fractions 4 and 5 turn strongly yellow, and fractions 6–9 weekly yellow. None of the compounds were identified, but the compound responsible for the coloration is probably identical with the above mentioned compound from furfuryl alcohol and furfuryl methyl ether having the same property. Since the compound is alkali stable, and is not found in the reaction product from dimethoxydihydrosilvan, we believe it to be a furan compound, which is autoxidized on standing.

(c). The distillate boiling at 104° is 1,1,2(or 3),4,4-pentamethoxypentane (VIII). [Calc. for C₅H₇(OCH₃)₅ (222.3): C 54.0; H 10.0; OCH₃ 69.8]. The compound showed no absorption band around 5.8 μ .

0.900 g of pentamethoxypentane (0.040 mole) was hydrolyzed and the hydrolysate treated with acetonedicarboxylic acid and methylamine hydrochloride as described above. The yield of methylmethoxytropolinone picrate was 0.600 g (36 %) (m. p. 132–136°). Crystallization from ethanol gave 0.500 g (m. p. 133–134°). (Found: C 46.6; H 4.6; N 13.6; OCH₃ 7.2).

Table 5. Data for the distillation of alkali-resistant compounds from furfuryl methyl ether.

Fraction (g)	B. p. °C	n_D^{25}	C	H	OCH ₃
1 (1.35)	70.5—73.0	1.4242	55.4	9.3	52.4
2 (1.52)	73.0—73.6	1.4236	55.0	9.6	51.5
3 (1.97)	73.6—76.0	1.4239	54.9	9.4	51.5
4 (2.02)	76.0—88.5	1.4256	54.8	10.1	54.4
5 (2.02)	88.5—90.3	1.4268	55.2	9.5	53.8
6 (2.06)	90.3—91.0	1.4262	55.1	9.6	55.3
7 (2.04)	91.0—91.5	1.4261	55.4	9.6	53.5
8 (1.99)	91.5—92.4	1.4258	55.1	9.4	53.7
9 (1.98)	92.4—98.6	1.4258	55.3	9.5	56.6
10 (1.89)	98.6—103.2	1.4243	54.8	9.9	65.4
11 (1.71)	103.2—104.0	1.4232	54.2	9.8	70.6
12 (0.91)	104.0	1.4231	54.6	10.4	68.5

The infrared spectrum of the picrate was identical with that of the picrate of the tropinone from trimethoxytetrahydrosilvan.

The yield of trimethoxytetrahydrosilvan, as estimated by the distillation curve, is 5.5 g (1.1 %), of pentamethoxypentane 4.7 g (0.7 %) and of unknown compounds 11.1 g (about 2.5 %).

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