

wood extract to be made up of one component with a sedimentation constant of 4.5×10^{-18} c.g.s. unit, whereas the sapwood extract was made up of two components with sedimentation constants of 4.5×10^{-18} and 1.2×10^{-18} c. g. s. unit (see Figs. 1 and 2). The two components were es-

pentosan content of the higher molecular-weight component of the sapwood is 8.9%.

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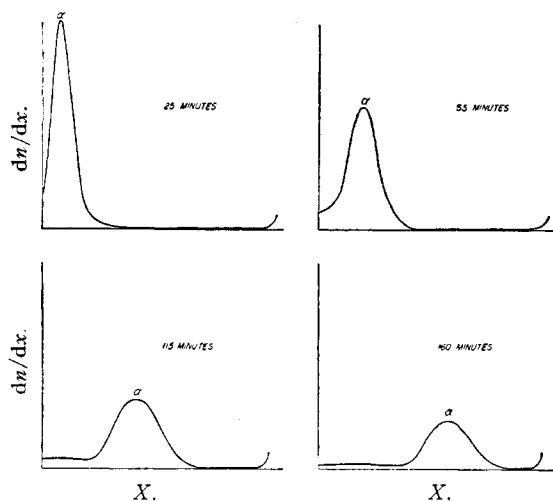


Fig. 1.—Sedimentation diagram of polysaccharide from the heartwood of Western larch at different times after the centrifuge had gained full speed: abscissa, distance from axis of rotation; ordinate, refractive index gradient; 25, 55, 115 and 160 minutes.

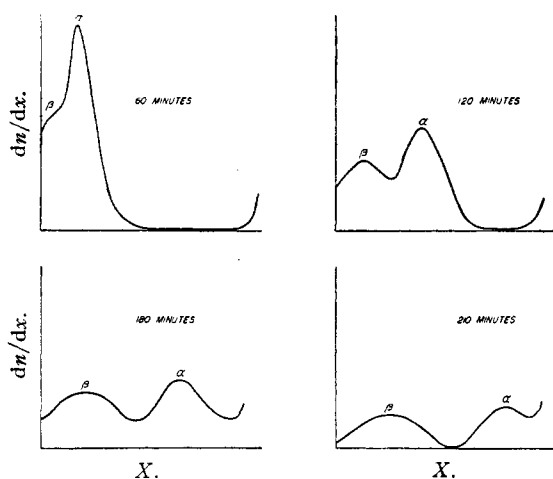


Fig. 2.—Sedimentation diagram of polysaccharide from the sapwood of Western larch at different times after the centrifuge had gained full speed: abscissa, distance from axis of rotation; ordinate, refractive index gradient; 60, 120, 180, and 210 minutes.

timated to be present in the proportions of 3:2, the component of higher molecular weight being present in the larger amount. If the higher molecular weight component of both extracts is the same material, as appears to be the case, the calculated

Peracetic Acid Oxidation of Thiol Esters

BY CHESTER J. CAVALLITO AND DOROTHY MCKENICA
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The preparation of the thiolsulfonates by per-acid oxidation of disulfides¹ suggested an attempt at preparation of α -keto sulfoxides and sulfones by a similar oxidation of thiol esters. Only one such compound, an aromatic α -ketosulfone, has been described briefly in the chemical literature.² Oxidation of thiol esters with peracetic or perbenzoic acids did not yield the α -keto sulfoxides or sulfones, but acid degradation products. The yields isolated are given in parentheses.

Peracetic acid in excess (6 moles to 1) in acetonitrile at 25° oxidized benzyl thiolbenzoate to two moles of benzoic acid (65%). Similarly, *p*-nitrobenzyl thiolbenzoate yielded *p*-nitrobenzoic (89%) and benzoic (95%) acids. Butyl thiolbenzoate gave benzoic acid (65%) and butanesulfonic acid (16%); the oxidative degradation did not proceed to the carbon atom of the aliphatic radical. Benzyl mercaptan yielded benzenesulfonic acid (93%); benzyl disulfide also gave the sulfonic acid with excess per-acid, but formed the thiolsulfonate as an intermediate. Benzyl benzoate was not oxidized under these conditions.

With one molar equivalent of per-acid, benzyl thiolbenzoate gave benzoic acid, (24% for two moles) considerable starting material (53%) and a trace of benzaldehyde. Benzyl thioacetate yielded starting product (35%) and benzyl benzyl thiolsulfonate (40%); excess per acid converted the latter to benzenesulfonic acid.

The oxidation of $RCH_2-S-COR'$ therefore proceeds to $R-COOH$ and $R'-COOH$ where R and R' are aromatic; to RCH_2SO_3H and $R'-COOH$ where R is aliphatic or where R is aromatic and R' is aliphatic. In the last instance, an intermediate is RCH_2SO_2SR , formed by either disproportionation of an intermediate α -keto sulfoxide or sulfone or from benzenesulfonic acid.³ In the first type, $RCH_2-SO-COR'$ may be first formed and rearranges to $RCHO$ and $R'-COSH$, both of which react further with per-acid yielding $R-COOH$, $R'-COOH$ and SO_2 .

Potassium permanganate or hydrogen peroxide in acetone did not oxidize the thiol esters at 25°. Otto and Lüders⁴ obtained benzoic acid and benzenesulfonic acid from permanganate oxidation of benzyl thiolbenzoate in acetic acid.

- (1) Small, Bailey and Cavallito, *THIS JOURNAL*, **69**, 1710 (1947).
- (2) Kohler and MacDonald, *Am. Chem. J.*, **22**, 219 (1899).
- (3) Fromm and Palma, *Ber.*, **39**, 3310 (1906).
- (4) Otto and Lüders, *ibid.*, **13**, 1285 (1880).

Experimental

Peracetic Acid Oxidations.—To 0.1 mole of compound to be oxidized dissolved in 100 cc. of acetonitrile was added with cooling an equal volume of acetonitrile solution of peracetic acid (prepared from either 40 or 70% peracetic acid). Cooling was continued for approximately thirty minutes after which the reaction mixture was allowed to stand at 25° for twenty-four hours. The mixture was concentrated under reduced pressure and under 40°, diluted with water and extracted with chloroform. Benzoic acids were removed from the chloroform by extraction with aqueous sodium bicarbonate solution; benzoic acid was separated from the *p*-nitro derivative by dissolving the former in petroleum solvents. The sulfonic acids were isolated as potassium salts from alcohol. Neutral esters or thioisulfonates remained in the chloroform after bicarbonate extraction.

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The Structure of Verbenalin

BY ASIMA CHATTERJEE¹ AND LLOYD M. PARKS

Since our work on the glucoside verbenalin was in progress when the recent paper by Karrer and Salomon² came to our attention, it appears desirable to report a part of our results at this time. We have isolated verbenalin from an American species, *Verbena stricta*, by a new and simplified procedure. Our analytical data for the glucoside are in agreement with Cheymol's formula, C₁₇H₂₄O₁₀,³ but the optical rotation differs.

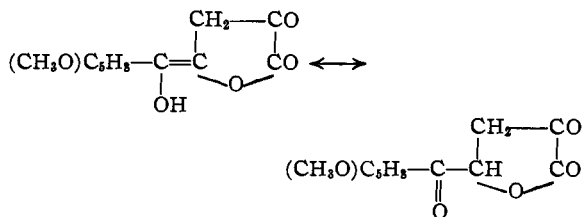
We have observed the same properties of verbenalin as reported by previous investigators, namely, a positive iodoform test, reduction of Fehling solution, and ammoniacal silver nitrate, no coloration with ferric chloride, and failure to yield carbonyl derivatives. Its saponification equivalent is lower than the theoretical value for one lactone group, indicating the presence of some other alkali-labile groups. The compound absorbs approximately one mole of bromine on titration but liberates it slowly on standing, which might indicate the presence of a labile enol group.

In contrast to Karrer's report,² verbenalin was reduced smoothly in the presence of Adams catalyst, absorbing two moles of hydrogen to yield a crystalline tetrahydroverbenalin, C₁₇H₂₈O₁₀, which gives no iodoform test nor color with ferric chloride, does not reduce Fehling solution, but does reduce ammoniacal silver nitrate. Our hydrogenated product, m. p. 173–174.5°, may be an isomer of the one, m. p. 195–196°, obtained with platinized Raney nickel, by Karrer.²

Emulsin hydrolysis of verbenalin at 23–25° and pH 4.3–4.6 produces the aglucone, verbenalol, C₁₁H₁₄O₅, in maximum yields of approximately 60%. Analytical data for this aglucone agree with that of Cheymol and Karrer except for

optical rotation. Verbenalol gives a positive iodoform test, reduces Fehling solution as well as hot aqueous copper acetate and ammoniacal silver nitrate; and, contrary to Karrer's observation, it gives immediately a strong violet color reaction with ferric chloride. Upon bromine titration it absorbs one mole of halogen which it liberates slowly on standing. Verbenalol also yields a di-2,4-dinitrophenylhydrazone, indicating the presence of two carbonyl groups; and on treatment with diazomethane yields an oily product which is not colored by ferric chloride; hence the presence of an enolic group in verbenalol must be assumed.

Emulsin hydrolysis of tetrahydroverbenalin produces tetrahydroverbenalol, C₁₁H₁₈O₆, (yield 60%), the m. p. of which, 123–124°, is considerably higher than that of Karrer's sample (102°), which was isolated from a mixture of reduction products of verbenalin.² Tetrahydroverbenalol gives no iodoform reaction nor coloration with ferric chloride; it does not reduce Fehling solution, but does reduce ammoniacal silver nitrate. It is indifferent to carbonyl reagents but yields a diacetate. The negative reaction with periodic acid² excludes the presence of an α -glycol grouping in its structure. The structure



for verbenalol appears to explain all of the data thus far available on the compound and its tetrahydro derivative. The sugar contained in the naturally occurring glucoside, which has been identified as glucose,³ may well be linked to the enolic hydroxyl group. Less probable is a structure containing the sugar in an α -enol lactone since it would fail to explain the positive iodoform test for the glucoside. Further work on oxidative degradation to clarify the structure of the C₅H₈ group and to confirm the above formula is in progress.

Experimental

Isolation of Verbenalin.—2-Kg. portions of dried, powdered *V. stricta* (collected near Madison, Wis.) were extracted with ether for two weeks in a Soxhlet apparatus. Verbenalin separated from the solution in the extraction flask, was filtered, washed with ether-acetone (1:1) and then dry acetone which removed most of the coloring and gummy matter. It was then decolorized with charcoal in alcohol and purified by several recrystallizations from alcohol and alcohol-ethyl acetate when colorless rhombic plates, m. p. 182–183° (dec.)⁴ were obtained; yields averaged 0.85%; $[\alpha]_D^{25}$ –171 to 172° (water); –165 to 166° (alcohol).

Anal. Calcd. for C₁₇H₂₄O₁₀: C, 52.57; H, 6.18; OCH₃, 7.99; mol. wt., 388; sapon. equiv., 388. Found: C,

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(2) P. Karrer and H. Salomon, *Helv. Chim. Acta*, **29**, 1544 (1946).

(3) J. Cheymol, *Bull. Soc. Chim.*, **5**, 633, 642 (1938).

(4) All melting points given are corrected.