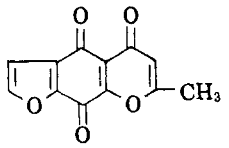
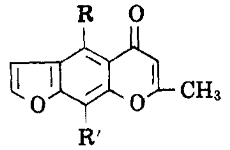
(2-methylfuro-4',5'-6,7-chromone-5,8-quinone) (I).[3] For the structure of the reaction product, which is phenolic in character (ferric chloride reaction), the choice lies between IIa and IIb. That formula IIa is correct could be seen from the fact that methylation with ethereal diazomethane (in the absence of methyl alcohol) could be effected with the formation of IIe. Chromones with hydroxyl groups in position 5 are very resistant toward ethereal diazomethane solutions,[4] this is believed to be due to chelation.[5] The photo-product is soluble in aqueous alkali, while the mono-hydroxy chromones with the hydroxyl group in position 5 are not.[4,6]



I



II

IIa, R = OCOPh, R' = OH
b, R = OH, R' = OCOPh
c, R = R' = OH
d, R = OH, R' = OCH$_3$
e, R = OCOPh, R' = OCH$_3$

IIe could also be obtained by the treatment of 5-hydroxy-8-methoxy-2-methylfour-4',5,'6,6-chromone (IId)[4] with benzoyl chloride in pyridine. A facile hydrolysis of IIa to IIc[7] using dilute hydrochloric acid was observed. The photoaddition of benzaldehyde to anthraquinone was tried without success.

EXPERIMENTAL

General remarks. The photoexperiments were carried out in Schlenk tubes[8] of Pyrex glass. The tubes were sealed while a stream of carbon dioxide was passing through. The benzene used was thiophene-free and dried over sodium. The ferric chloride tests were carried out by dissolving the substance in ethyl alcohol and adding ferric chloride in water.

Photochemical reaction between benzaldehyde and khellinquinone. Khellinquinone (I) (1.1 g., 1 mole) and freshly distilled benzaldehyde (1.5 g., 3 mole), in 30 ml. benzene, were exposed to sunlight for 60 days (Jan.-Feb.). At the end of the experiment, a yellow deposit (I is orange) was formed, filtered off, washed with benzene, and crystallized from ethyl alcohol. IIa forms almost colorless crystals m.p. 220° with decomposition, (yield, 0.7 g.). IIa is soluble in aqueous 10% sodium hydroxide, dissolves in concd. sulfuric acid with a yellow orange color, and gives a blue-green ferric chloride color reaction.

Anal. Calcd. for $C_{19}H_{12}O_6$: C, 67.8; H, 3.6. Found: C, 67.6; H, 3.5.

Action of diazomethane on IIa. To 1 g. of IIa was added an ethereal solution of diazomethane (from 6 g. of nitrosomethylurea). The reaction vessel was kept in the ice chest for 24 hr. The solid phase was filtered off and crystallized from ethyl alcohol as colorless crystals of IIe, m.p. 210°. Admixture with the product obtained as described below gave no depression, but on admixing with IIa, there was a depression in the m.p. to 190°. IIe is insoluble in 10% aqueous sodium hydroxide solution, soluble in concd. sulfuric acid with a yellow-orange color, and gives no color reaction with ferric chloride.

Anal. Calcd. for $C_{20}H_{14}O_6$: C, 68.6; H, 4.0. Found: C, 68.5; H, 3.9.

Benzoylation of IId. To 0.6 g. of IId in 10 ml. of pyridine (dried over potassium hydroxide and then distilled) was added about 1 g. of benzoyl chloride and the mixture was heated with shaking on a boiling water bath for 15 min. The mixture was left to cool and then acidified with 10% ice cold acetic acid. The deposit was filtered off, washed with water, and crystallized from ethyl alcohol as colorless crystals of IIe, m.p. 210°. It is insoluble in 10% aqueous sodium hydroxide and gives no color reaction with ferric chloride.

Anal. Calcd. for $C_{20}H_{14}O_6$: C, 68.6; H, 4.0. Found: C, 68.8; H, 4.1.

Hydrolysis of IIa. To 0.5 g. of IIa in 20 ml. of dioxane was added 15 ml. of hydrochloric acid (7.5 ml. of concd. hydrochloric acid of sp. gr. 1.18, mixed with 7.5 ml. water) and the solution was refluxed for 1 hr. The solution was allowed to cool and the product obtained was filtered off and crystallized from acetic acid as yellow crystals of IIc, m.p., 276°; admixture with an authentic sample[7] gave no depression.

Photochemical reaction between benzaldehyde and anthraquinone. A similar experiment was carried out as in the case of benzaldehyde and khellinquinone. Anthraquinone was recovered unchanged as proved by melting point, and mixed melting point.

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[3] A. Schönberg and N. Badran, *J. Am. Chem. Soc.*, **73**, 2960 (1951).

[4] A. Schönberg and G. Aziz, *J. Am. Chem. Soc.*, **75**, 3265 (1953).

[5] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 746 (1946).

[6] H. Schmid, *Helv. Chim. Acta*, **32**, 814 (1949).

[7] A. Schönberg and A. Sina, *J. Am. Chem. Soc.*, **72**, 3396 (1950).

[8] W. Schlenk and A. Thal, *Ber.*, **46**, 2840 (1913).

Stereochemistry of the Tropane Alkaloids. XI.[1] Oxidation of Four Epimeric Ecgoninols by Silver Oxide

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Received March 25, 1957

A recent paper of this series[2] dealt with the preparation and configurations[3] of 2β-hydroxymethyltropan-3α-ol and 2α-hydroxymethyltropan-3α-ol,

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[1] Part X, I. Vincze, J. Tóth, and G. Fodor, *J. Chem. Soc.*, in press.

[2] Ö. Kovács, I. Weisz, P. Zoller, and G. Fodor, *Helv. Chim. Acta*, **39**, 99 (1956).

[3] For stereochemical notations see Parts I and VI of this series: *J. Chem. Soc.*, 721 (1953) and 3504 (1955), respectively.

respectively. Oxidation of these together with the $2\beta,3\beta$ and $2\alpha,3\beta$-epimers described earlier[4,5] into the appropriate hydroxycarboxylic acids, *i.e.*, ecgonines, has been intended.[2] Up to that time (−) ecgonine and (+) ψ-ecgonine were known compounds but the third modification was known only as a racemate, while the fourth was unknown.

The synthesis of the hitherto unknown epimeric ecgonines has been attempted now. Hydrogenation of methyl tropinone-2-carboxylate leading to the third racemate[6] has been reinvestigated recently by Zeile and Schulz[7] as well as by Findlay.[8] Both German and American authors benzoylated the third racemate to a new (±) cocaine. Furthermore Findlay converted the third racemate into the fourth (±) ecgonine and (±) cocaine epimer ascribing simultaneously definite configurations to them. Synthesis of the optically active modifications by using optically active methyl tropinone-2-carboxylate as an intermediate has been outlined briefly.[8]

We now wish to record our experiments concerning oxidation of the four ecgoninols using a variety of reagents. Attempts at selective oxidations of a primary hydroxyl group leaving the unprotected secondary hydroxyl group intact are known to be unsuccessful even in the carbohydrate field.[9] Unfortunately, however, the reactants used for this purpose heretofore, as *e.g.* nitric acid, failed to give any definite product in reaction with 2β-hydroxymethyltropan-3β-ol. Use of silver oxide was rather promising, for this secured smooth conversion of vanillyl alcohol into vanillin.[9] Indeed ecgoninol hydrochloride gave on the steam bath with three moles of this reagent a mixture of the β-hydroxy acid together with some unchanged diol in 83% yield while the rest escaped identification.

A higher conversion has been achieved with ψ-ecgoninol, *i.e.* 2α-hydroxymethyltropan-3β-ol, which furnished 82% ψ-ecgonine. Unfortunately, however, neither the $2\beta,3\alpha$ nor the $2\alpha,3\alpha$ epimer gave positive results when oxidized, 93% of the latter being recovered unchanged while the former underwent oxidation (a silver mirror being formed) but only unchanged diol was obtained in 43% yield. That the rest did not show any spot in paper chromatography after treatment with Dragendorff's reagent may indicate destruction of the basic moiety in the molecule. Though the four epimers behave in a markedly stereospecific manner towards silver oxide, our original aim could not be achieved.

EXPERIMENTAL

Oxidation of ecgoninol into ecgonine. 2β-Hydroxymethyltropan-3β-ol hydrochloride[5] (415 mg., 0.002 mole) was dissolved in 12.5 ml. of *N* NaOH, then freshly prepared silver oxide from 1.02 g. of silver nitrate (0.006) was added and the whole immersed in a steam bath for 1.5 hr. with intermittent stirring. Meanwhile a silver mirror appeared on the walls of the flask. Then the reaction mixture was allowed to cool, the precipitate removed by filtration, the filtrate adjusted to *p*H 2 with concentrated hydrochloric acid, then decolorized (charcoal) and filtered again. The solution was evaporated to dryness and the residue taken up in 20 ml. of anhydrous ethanol. After repeated filtration and evaporation the remaining material was recrystallized fractionally from ethanol (10 ml.) and ether. The first crop, after recrystallization from anhydrous ethanol–ether amounted to 172 mg. (42%) and showed a m.p. of 243–245° and $[\alpha]_D^{20}$ −55.8 (H_2O, $c = 1.95$).

Anal. Calcd. for $C_9H_{16}O_3NCl$: C, 48.76; H, 7.27; ionic Cl, 15.99. Found: C, 49.12; H, 7.18; ionic Cl, 15.64.

By virtue of these data the compound proved to be identical with ecgonine hydrochloride.[11,12,13]

The second crop, precipitated by further addition of ether showed a m.p. of 267–269° and $[\alpha]_D^{20}$ −37.0 (H_2O, $c = 2.02$). It has been identified as the hydrochloride of 2β-hydroxymethyl-3β-hydroxytropane, the starting material.[5]

Number	Compound	R_F Values
1.	2β-Hydroxymethyltropan-3β-ol	0.49
2.	2α-Hydroxymethyltropan-3β-ol	0.53
3.	2β-Hydroxymethyltropan-3α-ol	0.38
4.	2α-Hydroxymethyltropan-3α-ol	0.63
5.	2β-Carboxy-3β-hydroxy-tropane	0.07
6.	2α-Carboxy-3β-hydroxy-tropane	0.05
7.	Reaction mixture resulting from oxidation of 1	0.07 0.49
8.	Reaction mixture resulting from oxidation of 2	0.05
9.	Reaction mixture resulting from oxidation of 3	0.40
10.	Reaction mixture resulting from oxidation of 4	0.62

Pseudoecgonine hydrochloride from "pseudoecgoninol" (2α-hydroxymethyltropan-3β-ol). 2α-Hydroxymethyltropan-3β-ol[5] hydrochloride, 415 mg. (0.002 mole), underwent oxidation

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[4] K. W. Rosenmund and F. Zymalhorsay, *Chem. Ber.*, **85**, 152 (1952).

[5] G. Fodor and Ö. Kovács, *J. Chem. Soc.*, 724 (1953); *cf.* Ö. Kovács, G. Fodor, and I. Weisz, *Helv. Chim. Acta*, **37**, 892 (1954).

[6] R. Willstätter, O. Wolfes, and O. Mäder, *Ann.*, **434**, 111 (1923).

[7] K. Zeile and W. Schulz, *Chem. Ber.*, **89**, 678 (1956).

[8] S. P. Findlay, *J. Org. Chem.*, **21**, 711 (1956).

[9] I. A. Pearl, *J. Am. Chem. Soc.*, **68**, 429 (1946).

[10] R. Lohmar and R. M. Goepp, Jr., in *Advances in Carbohydrate Chemistry*, Vol. IV, p. 226. Academic Press, N. Y. 1949; compare, however, with R. Bognár and L. Somogyi, *Szerves Kémiai Konferencia, Debrecen*, 1954, p. 179.

[11] C. Liebermann and F. Giesel, *Ber.*, **23**, 508 (1890).

[12] R. Willstätter and A. Bode, *Ann.*, **326**, 60 (1903).

[13] A. Einhorn, *Ber.*, **22**, 1495 (1889).

[14] J. Gadamer and T. Amenomiya, *Arch. Pharm.*, **242**, 9 (1904).

under the same conditions given above for the 2β-epimer to furnish, after recrystallization from dry ethanol-ether, a single crystalline product, 333 mg. (82%) of m.p. 234–236°, $[\alpha]^{20}_{\mathrm{D}}$ +20.9 (H_2O, *c* 1.87) which proved identical in every respect with[11,14] pseudoecgonine hydrochloride.

Anal. Calcd. for $C_9H_{16}O_3NCl$: C, 48.76; H, 7.27; ionic Cl, 15.99. Found: C, 48.65; H, 6.99; ionic Cl, 15.71.

Attempts to oxidize 2β-hydroxymethyltropan-3α-ol. The hydrochloride of the 2β,3α-diol, 415 mg. (0.002 mole) of m.p. 258–260° and $[\alpha]^{20}_{\mathrm{D}}$ −12.88° (H_2O, *c* 2.11), was treated with silver oxide exactly as given for the 2β,3β and 2β,3α epimers. A silver mirror separated while heating was in progress. The single crop of crystals amounted to 196 mg., which, after having been recrystallized from methanol and ether had a m.p. of 256–260°, $[\alpha]^{20}_{\mathrm{D}}$ −12.4° (H_2O, *c* 1.98), properties identical with those of the starting diol.

The brownish residue has been subjected to paper and cellulose powder chromatography. Unfortunately, no spot could be detected when the paper was treated with Dragendorff's reagent. This may justify the conclusion that the products of oxidation of basic character initially formed were subsequently destroyed by silver oxide, while an amount of the starting material remained unaffected.

Attempt to oxidize 2α-hydroxymethyltropan-3α-ol. Under strictly identical conditions, this so-called fourth epimer withstood any attempt to be oxidized with wet silver oxide in the alkaline medium. From such a reaction mixture 380 mg. (93%) of the starting material, of m.p. 171–172°, and $[\alpha]^{20}_{\mathrm{D}}$ 13.2 (H_2O) was recovered. No silver mirror formed during the reaction.

Separation of the four epimeric hydroxymethyltropan-3-ols by paper chromatography. Paper used: Whatman, No. 4. Solvent: 1-butanol: 0.043*N* ammonium hydroxide (1.5:1), descending. Temperature: 20°. Time: 8 hr. Developed by iodine vapors, and Dragendorff's reagent, respectively (5 min., 70°). Sample used: 30–40 γ.

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Derivatives of Sulfenic Acids. XXVIII. Ultraviolet Spectra of Diastereomers Obtained *via* Reactions of Sulfenyl Halides[1]

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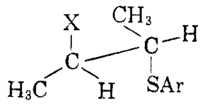
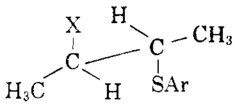
Received March 25, 1957

When 2,4-dinitrobenzenesulfenyl chloride or 2-nitro-4-carboxybenzenesulfenyl chloride add to the *cis* and *trans*-2-butenes, the diastereomeric racemates, I, I′ and II, II′ result; and acetolysis of these adducts yields the corresponding acetates, I-A, I′-A and II-A, II′-A (Ar-2, 4-dinitrophenyl or 2-nitro-4-carboxyphenyl).[3,4] Only one enantiomer of each racemate is shown.


I


II

I, X = Cl; Ar = 2,4-dinitrophenyl
I-A, X = Acetate; Ar = 2,4-dinitrophenyl
I′, X = Cl; Ar = 2-nitro-4-carboxyphenyl
I′-A, X = Acetate; Ar = 2-nitro-4-carboxyphenyl
II, X = Cl; Ar = 2,4-dinitrophenyl
II-A, X = Acetate; Ar = 2,4-dinitrophenyl
II′, X = Cl; Ar = 2-nitro-4-carboxyphenyl
II′-A, X = Acetate; Ar = 2-nitro-4-carboxyphenyl

The availability of the above compounds suggested the present investigation, whose purpose was to determine if the ultraviolet absorption spectra of the diastereomeric racemates would reveal any differences; and whether or not these could be correlated with the configurations of the respective racemates.

While the ultraviolet spectra of diastereomers have been investigated in only a few instances, some interesting correlations have been revealed. Thus, Hawthorne and Cram[5] assigned stereochemical configurations to certain substituted dinitroanilines on the basis of the relative intensities at the wave length of their major absorption band and also noted small differences in the positions of the absorption maxima for pairs of diastereomeric racemates. Cromwell and co-workers[6] correlated the stereochemistry of certain ethyleneimine ketones with their ultraviolet spectra; and, in a system more closely related to the present one, Freed and Sancier[7] found that the absorption maxima for solutions of iodine in the respective 2-butenes differed (*cis* = 295 mμ; *trans* = 297 mμ) but did not rationalize this difference.

The ultraviolet spectra of the compounds investigated in the present study are summarized in Table I. As expected, the acetates and chlorides of each system have very closely related spectra, since the chromophoric system in each chloride is but little changed in the conversion to the acetate. There is, however, a marked regularity in the displacements of the absorptions to longer wave lengths in the isomers obtained from *trans*-2-butene. Thus, in the first maximum, the product I, I-A, I′ and I′-A (derived from *cis*-2-butene) clearly absorb at shorter wave lengths than do II, II-A, II′ and

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[1] This study was supported, in part, by the Office of Ordnance Research, U. S. Army Contract DA-04-495-Ord. 306 and is abstracted from the Ph.D. dissertation of Anton J. Havlik, University of Southern California, 1954. For part XXVII, *cf. J. Chem. Ed.*, 33, 585 (1956).

[2] Atomic Energy Commission Predoctoral Fellow, 1951–53.

[3] A. J. Havlik and N. Kharasch, *J. Am. Chem. Soc.*, 78, 1207 (1956).

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[6] N. H. Cromwell, N. G. Barker, R. A. Wanke, P. J. Vanderhorst, F. W. Olson, and J. H. Anglin, *J. Am. Chem. Soc.*, 73, 1044 (1951).

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