applied only when the specific gravity is taken at 25°, for which temperature many urinometers are now adjusted. For an instrument graduated to give the specific gravity at 20° referred to water at 4° the factor to be used is 0.234. This was found by making a number of determinations of the specific gravity at the two temperatures and calculating the average coefficient of expansion. Neubauer's average factor is 0.233, based on urine at 15° referred to water at 0°. For the same temperature limits the results are practically identical, which indicates that for normal mixed urine the coefficient has a sharp definite value. and that it may be used as a control in certain kinds of analyses. Results of still greater value in practice may doubtless be secured through the exact determination of a factor for the solids, exclusive of the sodium chloride, that is, for the products of metabolic origin. A series of determinations in this direction is now in progress.

In any case the *exact* determination of the total solids by evaporation does not appear to be possible because of the uncertainty as to how the ammonia loss should be calculated.

My thanks are due to Mr. C. W. Brown, who made many of the determinations given above.

NORTHWESTERN UNIVERSITY,
CHICAGO, December, 1902.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

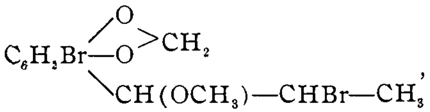
DERIVATIVES OF ISOSAFROL AND ISOAPIOL.

BY F. J. POND AND C. R. SIEGFRIED.

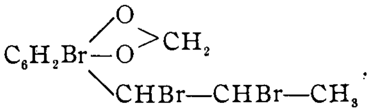
Received January 2, 1903.

IN a previous paper,[1] certain compounds were described which were found to result by the action of hot methyl and ethyl alcohols upon the bromine derivatives of anethol, isosafrol, ethyl isoeugenol and isoapiol; it was stated that these compounds are formed by the replacement of the bromine atom in the side-chain, which stands in the α-position to the benzene ring, by the methoxyl- and ethoxyl-groups. Thus, for example, a compound having the formula,

[1] Pond, Erb and Ford : This Journal, **24**, 327.



results on boiling monobromisosafrol dibromide,



with methyl alcohol. This compound separates from methyl alcohol in large, prismatic crystals, melting at 75° to 76.5°, and it was designated as the methyl alcohol addition-product of dibromisosafrol; it may perhaps be better termed α-methoxy-β-brom-dihydro-bromisosafrol. The analogous ethyl alcohol product was also described. It was likewise shown that corresponding methyl and ethyl alcohol products are formed in a similar manner from anethol dibromide, monobromanethol dibromide, isosafrol dibromide and ethyl isoeugenol dibromide. The alcohol products resulting from anethol and monobromanethol dibromides, isosafrol and ethyl isoeugenol dibromides, having the general formula,

$$R—CH(OR')—CHBr—CH_3,$$

were found to be readily converted by sodium methylate or alcoholic potash into ketones,

$$R—CO—CH_2—CH_3,$$

while the compounds obtained from monobromisosafrol dibromide are remarkably stable towards alkaline reagents, and they do not yield ketones on treatment with sodium alcoholate. The formation of the ketones from the first class of compounds is due to the elimination of the bromine atom in the β-position as hydrogen bromide, and the resulting unsaturated ether is then converted into a saturated ketone by hydrolysis and subsequent molecular rearrangement. In the second class of compounds, the β-bromine atom is not removed by the ordinary alkaline reagents.

Some months after the completion of the work described in the previous paper, Auwers and Müller[1] published an article on certain derivatives of the bromides of eugenol and isoeugenol. These

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[1] Auwers and Müller: *Ber. d. chem. Ges.*, **35**, 114.

chemists found that the bromine derivatives of eugenol, which may be represented by the general formula,

$$\mathrm{R{-}CH_2{-}CHBr{-}CH_2Br},$$

are not changed by the treatment with alcohols, aqueous acetone, sodium acetate, organic bases, etc., and that they show no abnormal reactions, but possess the character of ordinary phenols. On the other hand, however, the bromides of isoeugenol, having the formula,

$$\mathrm{R{-}CHBr{-}CHBr{-}CH_3},$$

are at once changed by cold methyl or ethyl alcohol, aqueous acetone and sodium acetate, one atom of bromine being eliminated and replaced by the corresponding radical. In every case the bromine atom which is removed is the one standing in the α-position to the benzene radical; the second or β-bromine atom does not enter into the reaction even at high temperatures or when the reagents, such as sodium acetate, are employed in a large excess. The formation of these compounds is represented by the formulas,

$$\mathrm{R{-}\underset{\alpha}{C}HBr{-}\underset{\beta}{C}HBr{-}CH_3 \rightarrowtail R{-}\underset{\alpha}{C}H(R'){-}\underset{\beta}{C}HBr{-}CH_3}.$$

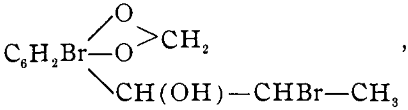
According to Auwers, therefore, the bromides of isoeugenol possess the character of pseudo-phenols, and in general the bromides of para-alkyl phenols, which contain bromine atoms in the α- and β-positions, react as pseudo-phenols.

A further point of considerable interest in Auwers's work is that when the ethers or alcohols, resulting by the treatment of isoeugenol dibromide or tribromide, are heated with alcoholic sodium methylate, the β-bromine atom is not eliminated as hydrogen bromide, as was found to be the case with the compounds derived from the bromides of isoeugenol ethers investigated in this laboratory, but it is replaced by the methoxyl-group; this reaction gives rise to ethers of glycols as is represented by the equation,

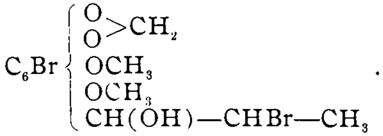
$$\mathrm{R{-}\underset{\alpha}{C}H(OCH_3){-}\underset{\beta}{C}HBr{-}CH_3 + NaOCH_3 = NaBr + R{-}CH(OCH_3){-}CH(OCH_3){-}CH_3}.$$

It will be readily seen from the foregoing that Auwers's work is more or less intimately related with the line of investigation which has been conducted in this laboratory for the past three years, the chief difference being that Auwers's researches were carried on with isoeugenol, a compound containing the free phenolic group, while our work is confined to the ethers of isoeugenol and of other propenyl phenols as anethol, isosafrol and isoapiol. This difference in the constitution of the compounds appears to exert a considerable influence upon the reactions of the substances derived from them, since in no case have we observed the formation of ethers of glycols as described by Auwers.

The experimental work described in this paper is a continuation of our investigations on the action of alcohols and aqueous acetone upon the bromides of isosafrol and isoapiol. From monobromisosafrol dibromide we have prepared a new alcohol,



its methyl and ethyl ethers, together with its acetyl and benzoyl derivatives; the same series of compounds is also obtained from monobromisoapiol dibromide, the new alcohol having the formula,

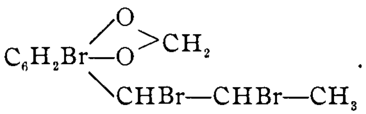


$$C_6Br\left\{\begin{array}{l} \begin{matrix}O\\O\end{matrix}\!>CH_2 \\ OCH_3 \\ OCH_3 \\ CH(OH)-CHBr-CH_3 \end{array}\right. .$$

From this alcohol a new ketone has also been obtained.

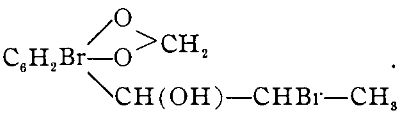
EXPERIMENTAL.

Monobromisosafrol Dibromide,[1]



This compound is readily prepared as previously described by treating an ethereal solution of isosafrol with two molecular proportions of bromine. It separates from a mixture of acetone and ether in colorless crystals, melting at 110° to 111°.

α-Oxy-β-brom-dihydro-bromisosafrol,



A solution of 10 grams of monobromisosafrol dibromide in 50 cc.

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[1] Pond, Erb and Ford: This Journal, **24**, 340.

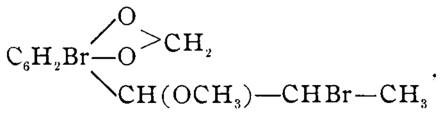
of acetone was heated to boiling and then treated with 15 cc. of water; the aqueous acetone solution was boiled in a reflux apparatus on the water-bath for two hours. The solution at first assumed a red color, which gradually became colorless. On completion of the reaction, the product was poured into an evaporating dish, and, after the evaporation of the acetone, a compound separated as a yellow-colored oil; after standing for about twelve hours, this oil solidified to a white, waxy substance, which was filtered, washed well with water and pressed on a porous plate. The crude compound is exceedingly soluble in alcohol and ether, hence it is best to crystallize first from acetone and to recrystallize from alcohol; it separates from these solvents in beautiful, large crystals, which melt at 89°.

Analysis gave the following results: Calculated for $C_{10}H_{10}O_3Br_2$, C, 35.50; H, 2.95; Br, 47.33. Found, C, 35.75, 35.78; H, 3.21, 3.07; Br, 47.23.

When this compound is boiled with alcoholic potash or sodium methylate, bromine is eliminated; on acidifying the reaction-product with hydrochloric acid and then adding water, an oil is formed. It was expected that this oil would exhibit the ordinary reactions of a ketone, but it failed to yield an oxime or semicarbazone, and its examination must be continued.

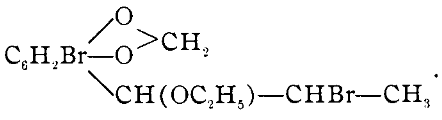
The methyl and ethyl ethers of the foregoing alcohol were described in a previous paper, but they will be briefly reviewed here for sake of completeness.

α-Methoxy-β-brom-dihydro-bromisosafrol,



is formed when a solution of monobromisosafrol dibromide in methyl alcohol is boiled for a short time. It crystallizes from methyl alcohol in large prisms, melting at 75° to 76.5°.

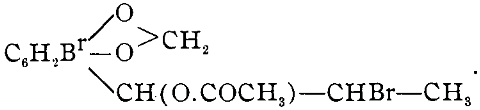
α-Ethoxy-β-brom-dihydro-bromisosafrol,



obtained by boiling a solution of isosafrol tribromide in ethyl alcohol, crystallizes from alcohol in large crystals, and melts at 58° to 60°.

Boiling, concentrated sodium alcoholate is without action upon these two ethers.

Acetate of α-Oxy-β-brom-dihydro-bromisosafrol,

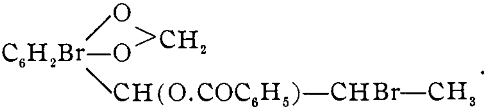


This compound is formed when a solution of 3 grams of potassium acetate in 5 cc. of glacial acetic acid is added to a solution of 10 grams of monobromisosafrol dibromide in 15 cc. of glacial acetic acid, and the whole is boiled for about five minutes.

The cold reaction-product is then poured into water; the compound separates as an oil, which solidifies after standing for about twelve hours. It is crystallized from alcohol, dried on a porous plate, and recrystallized from ethyl acetate; it separates from the latter solvent in fine, white needles, which melt at 73° to 74°.

Analysis gave the following results: Calculated for $C_{12}H_{12}O_4Br_2$, C, 37.89; H, 3.16. Found, C, 37.97, 37.63; H, 3.22, 3.26.

Benzoate of α-Oxy-β-brom-dihydro-bromisosafrol,

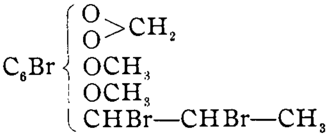


In order to prepare this benzoyl derivative of the alcohol, Einhorn and Hollandt's process was employed, since the ordinary Schotten-Baumann method employs alkali, which would lead to a decomposition of the alcohol.

Five grams of α-oxy-β-brom-dihydro-bromisosafrol were dissolved in 15 grams of pyridine, and 3 grams of benzoyl chloride were added slowly, with constant shaking; the mixture was allowed to stand during twenty-four hours, and then poured into dilute sulphuric acid (1:5). The benzoyl derivative separated at first as an oil, but solidified after repeated washing with dilute acid and water, and was crystallized from a mixture of ether and acetone; it forms long, white crystals, melting at 142° to 143°. It is readily soluble in the usual solvents.

Analysis gave the following results: Calculated for $C_{17}H_{14}O_4Br_2$, C, 46.15; H, 3.16. Found, C, 46.27, 46.10; H, 3.24, 3.21.

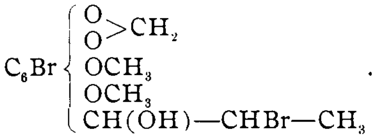
Monobromisoapiol Dibromide,



$$C_6Br\left\{\begin{array}{l} \begin{matrix}O\\O\end{matrix}\!>CH_2 \\ OCH_3 \\ OCH_3 \\ CHBr—CHBr—CH_3 \end{array}\right.$$

prepared as previously described[1] by the action of two molecular proportions of bromine upon an ethereal solution of isoapiol, crystallizes from acetone and melts at 120°.

α-Oxy-β-brom-dihydro-bromisoapiol,



$$C_6Br\left\{\begin{array}{l} \begin{matrix}O\\O\end{matrix}\!>CH_2 \\ OCH_3 \\ OCH_3 \\ CH(OH)—CHBr—CH_3 \end{array}\right. .$$

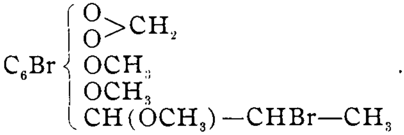
Twenty grams of monobromisoapiol dibromide were dissolved in 100 cc. of acetone and treated with 30 cc. of water; after boiling for two hours in a reflux apparatus, the acetone was allowed to evaporate and the oily residue was washed well with water. The oil gradually solidified, was washed, dried, and crystallized from alcohol; it separated in large, well-defined crystals, melting at 85° to 86°.

The compound is readily soluble in the usual solvents. When boiled with alcoholic potash, one atom of bromine is removed and a new compound is formed, which will be subsequently described.

Analysis gave the figures: Calculated for $C_{12}H_{14}O_5Br_2$, C, 36.18; H, 3.52; Br, 40.20. Found, C, 36.21, 35.98; H, 3.61, 3.31; Br, 40.34.

The methyl and ethyl ethers of the above-mentioned alcohol are easily obtained by boiling a solution of isoapiol tribromide in methyl or ethyl alcohol.

α-Methoxy-β-brom-dihydro-bromisoapiol,



$$C_6Br\left\{\begin{array}{l} \begin{matrix}O\\O\end{matrix}\!>CH_2 \\ OCH_3 \\ OCH_3 \\ CH(OCH_3)—CHBr—CH_3 \end{array}\right. .$$

A solution of 20 grams of monobromisoapiol dibromide in 50 cc.

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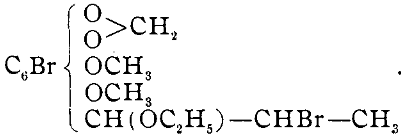
[1] See Pond, Erb and Ford : This Journal, **24**, 343.

of methyl alcohol is boiled for a few minutes and then poured into a crystallizing dish; the compound separates in large crystals, which melt at 92° to 93°.

Analysis gave: Calculated for $C_{13}H_{16}O_5Br_2$, C, 37.86; H, 3.88; Br, 38.83. Found, C, 38.02, 38.01; H, 3.90, 3.99; Br, 38.78, 38.85.

α-Ethoxy-β-brom-dihydro-bromisoapiol,



$$C_6Br\left\{\begin{array}{l}\begin{array}{l}O\\O\end{array}>CH_2\\OCH_3\\OCH_3\\CH(OC_2H_5)-CHBr-CH_3\end{array}\right. .$$

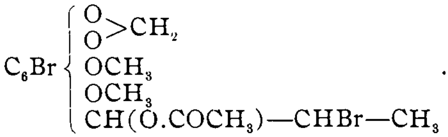
Twenty-eight grams of monobromisoapiol dibromide were dissolved in ethyl alcohol, and the solution was boiled for ten minutes; on cooling, this compound separated in large crystals, melting at 72° to 73°.

In our previous communication, this compound was described as an oil, and at that time it was impossible to induce the substance to solidify; now, however, we find no difficulty in obtaining a crystalline product at once. We are unable to find a satisfactory explanation for this difference in the behavior of the substance, unless we attribute it to a slightly purer isoapiol tribromide.

The compound was analyzed with the following results: Calculated for $C_{14}H_{18}O_5Br_2$, C, 39.43; H, 4.22. Found, C, 39.59, 39.20; H, 4.00, 4.05.

Hot, concentrated solutions of alcoholic potash and sodium methylate are without action upon these ethers.

Acetate of α-Oxy-β-brom-dihydro-bromisoapiol,



$$C_6Br\left\{\begin{array}{l}\begin{array}{l}O\\O\end{array}>CH_2\\OCH_3\\OCH_3\\CH(O.COCH_3)-CHBr-CH_3\end{array}\right. .$$

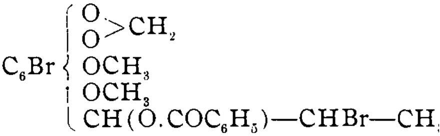
A hot solution of 2.5 grams of potassium acetate in 5 cc. of glacial acetic acid was added slowly, and with shaking, to a warm solution of 10 grams of monobromisoapiol dibromide in 15 cc. of glacial acetic acid, and the mixture was brought to a boiling temperature.

The cold reaction-product was then poured into water, extracted with ether, and the ethereal solution washed with water, dried over calcium chloride, filtered and the ether allowed to evaporate.

The substance remained as an oil, which solidified slowly; it was crystallized from ether and melted at 114° to 115°.

Analysis for carbon and hydrogen gave: Calculated for $C_{14}H_{16}O_6Br$, C, 38.18; H, 3.63. Found, C, 37.89, 38.18; H, 3.90, 3.58.

Benzoate of α-Oxy-β-brom-dihydro-bromisoapiol,



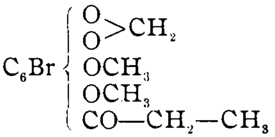
$$C_6Br\begin{cases}\begin{smallmatrix}O\\O\end{smallmatrix}\!>CH_2\\ OCH_3\\ OCH_3\\ CH(O.COC_6H_5)—CHBr—CH_3\end{cases}$$

This ester was obtained according to the Einhorn-Hollandt method of preparing benzoyl derivatives.

Five grams of α-oxy-β-brom-dihydro-bromisoapiol were dissolved in 15 cc. of pyridine and treated with 3 grams of benzoyl chloride, which was added gradually. After standing during twenty-four hours, the reaction-mixture was poured into dilute sulphuric acid (1 : 5), and allowed to remain until the oil, which at first separated, had solidified; the solid was then filtered, washed with dilute acid and water, and crystallized from alcohol. It separates in well-defined crystals, which melt at 117° to 118°.

The following figures were obtained by analysis: Calculated for $C_{19}H_{18}O_6Br_2$, C, 45.41; H, 3.58. Found, C, 45.14, 45.13; H, 3.64, 3.44.

α-Keto-dihydro-bromisoapiol,



$$C_6Br\begin{cases}\begin{smallmatrix}O\\O\end{smallmatrix}\!>CH_2\\ OCH_3\\ OCH_3\\ CO—CH_2—CH_3\end{cases}$$

Although the ethers of α-oxy-β-brom-dihydro-bromisoapiol are not affected by boiling with concentrated solutions of alcoholic potash or sodium methylate but, in fact, separate from these solutions on cooling and show their original melting-points, nevertheless the free alcohol itself is quite readily changed by the action of hot alcoholic potash. A similar circumstance was noted in the behavior of the derivatives from isosafrol as described above. The compound obtained from the α-oxy-isosafrol derivative is an oil, while that formed from the α-oxy-isoapiol derivthe acetate prepared from olive oil. It was thought that if a relatively small amount of maize oil were to be mixed with an oil known to contain phytosterol, it would be possible to secure by recrystallization of the acetates a portion whose melting-point would approach that of sitosterol acetate. The following trials were therefore made.

A pure cottonseed oil, a cottonseed oil containing 10 per cent. of maize oil, and one containing 20 per cent. of maize oil were extracted, using 50 gram portions, by boiling twenty minutes at a reflux condenser with 100 cc. of 95 per cent. alcohol. The mixtures were then run into separatories and left over night. The clear alcoholic layer was drawn off, boiled fifteen minutes with 75 cc. of half normal alcoholic potash, evaporated to dryness and the residue dissolved in 40-50 cc. of water. The cooled soap solution was shaken out with 75 cc. of ether and 3 cc. of alcohol, and the extract was washed three times with water and evaporated. The yield by this process, which was not expected to give complete extraction, was as follows: Pure cottonseed oil, 0.095 per cent.; 10 per cent. maize oil, 0.12 per cent.; 20 per cent. maize oil, 0.164 per cent.

The crystals obtained were acetylated without further purification by boiling one hour with an excess of acetic anhydride in a beaker covered with a watch-glass containing a little water. The excess of anhydride was evaporated on the water-bath and the acetates recrystallized from alcohol. In recrystallizing, the acetates were dissolved in hot 95 per cent. alcohol and water was then added drop by drop as long as the solution remained clear after shaking; as soon as there were indications of permanent opalescence a few drops of alcohol were added until the solution was perfectly clear. The beaker was then set aside and the crystals subsequently formed were filtered off, dried at 100° C. and the melting-point determined. Proceeding in this way the melting-points shown on the sixth, and subsequent, crystallization were: Pure cottonseed, 120°-121°; 10 per cent. maize, 121.5°-122.5°; 20 per cent. maize, 124°-125°. By dissolving the acetates in hot 95 per cent. alcohol just sufficient for solution and then chilling, there was obtained from the 20 per cent. oil after four crystallizations a portion which showed the melting-point 126°-127°; the melting-point of the acetate from the 10 per cent. oil was unchanged.

The crystals deposited on slow cooling from 95 per cent. alcohol were, in the case of pure cottonseed, transparent flat needles; the 20 per cent. maize oil gave crystals which beside these needles, showed an opaque, white, and more granular form; the crystals from the 10 per cent. oil resembled those from the pure cottonseed oil.

Portions of the crystals obtained from the dilute alcohol, as described above, were allowed to crystallize from a little 95 per cent. alcohol on glass slides and examined microscopically. All three acetates showed massed crystals in branching coral forms and also long narrow plates resembling the crystals of phytosterol and of sitosterol. There seemed to be less difference in the crystal forms as thus examined than appeared to the naked eye in the manner of growth of the crystals when slowly deposited.

It would seem that the above test will detect the addition of 10 per cent. of an oil containing sitosterol to an oil carrying phytosterol. While maize oil is the only commercial oil in which sitosterol has so far been definitely reported, Bömer and Winter[1] have obtained acetates melting at 128° and above from linseed, rapeseed and sesame oils; it seems probable that sitosterol is present in more oils than has hitherto been supposed and consequently that the test can only be regarded as conclusive evidence of the presence of maize oil when the analytical constants show the absence of other adulterants.

As the melting-point varies with the method employed, it will be advisable for the operator to determine the melting-point of phytosterol acetate according to the method he himself uses. The above values were determined in straight narrow tubes attached to the bulb of an Alverginat thermometer and suspended in a test-tube of sulphuric acid. This was in turn suspended in a 100 cc. flask about two-thirds full of acid. The flask was supported about an inch above an iron plate heated by a small Bunsen flame. The melting-point was approached fairly rapidly and when within 2° or 3°, the rate of heating was reduced to about 0.2° per minute. The value obtained by Bömer and Winter for the phytosterol acetate from cottonseed oil is 123°-124°, but it may be stated that the values obtained by Bömer for the melting-point of phytosterol are rather higher than those usually reported.

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[1] *Ztschr. Unter. Nahr. u. Genus.*, (1898), p. 81.

ON THE RELATION OF THE SPECIFIC GRAVITY OF URINE TO THE SOLIDS PRESENT.

BY J. H. LONG.

Received December 29, 1902.

ATTEMPTS have been made several times to establish a relation between the specific gravity of normal urine and the weight of solids dissolved in the secretion. Such efforts are naturally based on the assumption that while the solids must vary, the variations remain within rather narrow limits and the two most important constituents must change in the same direction. These two important substances are urea and sodium chloride, and the specific gravity observed depends largely on the weight of these bodies present.

From early experiments of Trapp, Haeser and others, repeated later by Neubauer,[1] the relation appeared in general to be definite enough to warrant the use of the so-called coefficient of Haeser in making an approximate estimation of the urine solids from an exact determination of the specific gravity. The direct estimation of solids by evaporation is apparently easy, but unfortunately is liable to an error due to the partial decomposition of urea into ammonium cyanate and that into ammonia and carbonic acid. In addition to this, there is a loss on account of the slightly stable ammonium salts present, which fact is generally overlooked, although its importance is as great as that of the loss from the urea, in some cases. Unless a correction is made for these losses, the error in the final result is rather large, in fact usually larger than is the difference between the true result and that obtained by applying the coefficient of Haeser.

As this is a point of no little importance, I have recently undertaken a new determination of the urinary solids along with the corresponding specific gravities, both determinations being made as accurately as possible. The solid residue was found by the method originally suggested by Neubauer. About 5 grams of urine are evaporated in a porcelain boat which is placed in a horizontal glass tube passing through a steam-bath. The glass tube is connected with a small flask containing standard sulphuric acid in such a manner that a current of dried air may be aspirated through the whole apparatus and carry evolved products into the

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[1] *Ztschr. anal. Chem.*, 1, 166.

standard acid. A subsequent titration with standard alkali and methyl orange shows how much acid has been neutralized by ammonia from the evaporated urine. Three to four hours are given to each evaporation, after which the residue in the boat is allowed to stand about two hours over sulphuric acid before weighing. Neubauer suggested to calculate the ammonia absorbed by the dilute standard acid to urea and add this to the weight of the residue. This has been done in the urine evaporations given below, although the method is not strictly correct, as will be pointed out.

The specific gravities were found by means of a small pycnometer and at a temperature maintained at 25°, with a variation within 0.1°. For possible practical applications, 25° is a much more suitable temperature than is 15° or even 20°. The results are referred to water at 4° as unity and are all given below.

Some preliminary experiments were made to determine the loss in evaporating solutions containing pure urea and certain salts in proportions corresponding to those obtaining for urine. In the first of these I took, with water enough to make about 4 cc.:

	(*a*).	(*b*).
NaCl	0.0930	0.0708
K_2SO_4	0.0077	0.0059
CON_2H_4	0.1467	0.1117
	0.2474	0.1884
Residue recovered	0.2430	0.1851
Urea from ammonia	0.0052	0.0037
	0.2482	0.1888

In the first case, the loss of 5.2 mg. of urea calculated from the ammonia is 3.5 per cent. of the urea present or 2.1 per cent. of the solids. In the second case, 3.7 mg. amounts to 3.3 per cent. of the whole urea, or 2 per cent. of the total solids. Very similar results were found in other tests and need not be given in detail. In the following experiments the effect of a phosphate was determined. With water enough to make about 3.5 cc. in each case, I took:

	(*c*).	(*d*).
NaCl	0.1126	0.0881
K_2SO_4	0.0080	0.0101
HNa_2PO_4	0.0120	0.0120
CON_2H_4	0.1526	0.1927
	0.2852	0.3029

The evaporation was continued three and a half hours, and the ammonia was caught as before.

Recovered directly	0.2830	0.2991
Loss	0.0022	0.0038

The ammonia evolved was found in (*c*) to be equal to 0.5 cc. of N/4 acid and in (*d*) to 0.6 cc. of N/4 acid. Calculating this as urea would more than account for the loss. In this case, however, a part of the carbonic acid from the urea decomposition is held by the alkali phosphate. In (*c*) the total loss was 14.4 mg. per gram of urea, or 1.44 per cent. of the total urea. In (*d*) the loss was 19.2 mg. per gram of urea or 1.92 per cent. of the urea present. These losses are about one-half as great as they were in the absence of the alkali phosphate.

Since the urine is commonly slightly acid and probably from the presence of the dihydrogen phosphate, two further evaporations were made with known amounts of this salt present. It was produced by addition of N/10 sulphuric acid to a solution of the disodium salt. The weights taken, with water enough to make up 4.5 cc., were:

	(*e*).	(*f*).
NaCl	0.1046	0.1053
K_2SO_4	0.0099	0.0100
Na_2SO_4	0.0060	0.0060
H_2NaPO_4	0.0100	0.0100
CON_2H_4	0.1893	0.1900
	0.3198	0.3213
Recovered directly	0.3171	0.3174
Loss	0.0028	0.0039
The ammonia evolved calculated as urea gives	0.0023	0.0037

In such cases, therefore, it seems perfectly proper to add urea to correct the evaporation loss, and the presence of the salts does not appear to increase this appreciably. The decomposition with alkaline phosphate present is probably the same, but the ammonia only is fully liberated.

Below are given the results of fifty-two determinations on the urine of six persons. The samples taken for the tests did not represent the excretion of the whole day but were chosen to represent extreme cases, as far as possible, as the main object of the investigation was to determine the limits of variations. From other investigations, the average amounts of urea and ammonia excreted by the same individuals, under the same general conditions, had been determined. The urea amounted to 28 grams per liter and the ammonia to 650 mg. per liter. All the tests were made on perfectly fresh urine, from individuals in normal health, consuming an average meat, vegetable and bread diet.

No.	Sp. gr. $\frac{25^{\circ}}{4}$	Solids in grams per liter.	Loss as urea, grams per liter.	Multiplication factor.
1	1.0199	51.57	2.36	0.259
2	1.0207	51.19	2.95	0.247
3	1.0206	52.33	2.37	0.254
4	1.0189	44.28	2.28	0.234
5	1.0209	53.70	2.14	0.257
6	1.0215	53.10	1.72	0.247
7	1.0227	61.93	2.89	0.272
8	1.0217	53.51	2.46	0.247
9	1.0224	56.54	2.13	0.252
10	1.0180	53.84	2.51	0.299
11	1.0252	66.05	2.56	0.262
12	1.0251	63.54	2.10	0.253
13	1.0226	57.19	1.71	0.253
14	1.0231	60.00	1.95	0.260
15	1.0236	57.38	1.76	0.243
16	1.0236	62.82	2.35	0.266
17	1.0248	59.90	2.74	0.242
18	1.0279	70.73	1.75	0.254
19	1.0230	59.31	1.70	0.258
20	1.0279	75.21	1.96	0.270
21	1.0223	57.48	2.09	0.258
22	1.0177	43.13	1.60	0.244
23	1.0231	63.06	1.92	0.273
24	1.0228	58.37	2.15	0.256
25	1.0284	75.55	1.67	0.266
26	1.0256	73.26	2.34	0.288
27	1.0246	59.75	1.93	0.243
28	1.0191	44.98	2.00	0.235
29	1.0317	79.29	2.31	0.250
30	1.0118	30.02	0.97	0.254
31	1.0237	63.45	4.53	0.268
32	1.0207	51.06	1.73	0.247
33	1.0291	70.90	4.19	0.244
34	1.0243	62.41	2.81	0.257
35	1.0140	37.81	2.01	0.270
36	1.0217	56.56	2.40	0.261
37	1.0225	59.29	2.75	0.264

No.	Sp. gr. $\frac{25^{\circ}}{4}$	Solids in grams per liter.	Loss as urea, grams per liter.	Multiplication factor.
38	1.0165	45.13	2.49	0.274
39	1.0212	60.01	3.64	0.283
40	1.0155	43.08	2.91	0.278
41	1.0247	62.74	1.62	0.254
42	1.0113	33.47	2.26	0.296
43	1.0161	44.72	2.03	0.277
44	1.0201	53.46	1.61	0.266
45	1.0231	60.95	2.38	0.264
46	1.0225	55.47	0.98	0.242
47	1.0221	56.19	1.83	0.254
48	1.0120	31.69	1.56	0.264
49	1.0160	41.84	1.60	0.261
50	1.0215	53.98	1.70	0.251
51	1.0267	68.91	1.17	0.258
52	1.0160	41.26	2.12	0.258
Mean,	1.0215	55.83	2.19	0.260

The evaporation losses calculated as urea, from the ammonia evolved, are seen to be far greater with the urine than with the artificial mixtures. With an average of 28 grams of urea in the urine the mean loss is evidently about 8 per cent. of this content. While as a matter of convenience it is satisfactory to calculate the loss as urea, a little consideration will show that a part of it must come from other sources. In the evaporation, part of the ammonia present, and possibly sometimes all of it, is driven off and this may be considered as combined as some organic salt and possibly partly as carbonate. In one case the loss would be less and in the other greater than that found by calculation as urea. The usual method of calculation probably represents the average loss, and this has been included in the figures representing the total solids in column 3.

The correspondence between high specific gravity and high solids is a fairly good one in most cases, as shown by the factor in the last column. representing the so-called Haeser coefficient for the temperature of 25°. This factor is obtained by dividing the last three figures of the specific gravity into the weight of solids found. In most cases the variations are not great from the mean value of 0.260, but in Nos. 4, 10, 26, 28, and 42 the divergence is much greater than given by Neubauer. For the *mixed* day's urine the results would be much closer and in any such case the factor 0.260 would not be far from the truth. This factor can be applied only when the specific gravity is taken at 25°, for which temperature many urinometers are now adjusted. For an instrument graduated to give the specific gravity at 20° referred to water at 4° the factor to be used is 0.234. This was found by making a number of determinations of the specific gravity at the two temperatures and calculating the average coefficient of expansion. Neubauer's average factor is 0.233, based on urine at 15° referred to water at 0°. For the same temperature limits the results are practically identical, which indicates that for normal mixed urine the coefficient has a sharp definite value, and that it may be used as a control in certain kinds of analyses. Results of still greater value in practice may doubtless be secured through the exact determination of a factor for the solids, exclusive of the sodium chloride, that is, for the products of metabolic origin. A series of determinations in this direction is now in progress.

In any case the *exact* determination of the total solids by evaporation does not appear to be possible because of the uncertainty as to how the ammonia loss should be calculated.

My thanks are due to Mr. C. W. Brown, who made many of the determinations given above.

NORTHWESTERN UNIVERSITY,
CHICAGO, December, 1902.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

DERIVATIVES OF ISOSAFROL AND ISOAPIOL.

BY F. J. POND AND C. R. SIEGFRIED.

Received January 2, 1903.

IN a previous paper,[1] certain compounds were described which were found to result by the action of hot methyl and ethyl alcohols upon the bromine derivatives of anethol, isosafrol, ethyl isoeugenol and isoapiol; it was stated that these compounds are formed by the replacement of the bromine atom in the side-chain, which stands in the α-position to the benzene ring, by the methoxyl- and ethoxyl-groups. Thus, for example, a compound having the formula,

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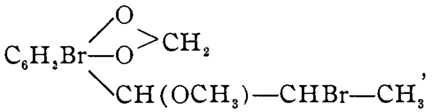
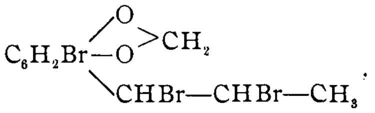
[1] Pond, Erb and Ford : This Journal, **24**, 327.



$$C_6H_2Br\begin{array}{l} \diagup O \\ -O \end{array}\!\!>CH_2 \qquad \begin{array}{l} \\ \diagdown CH(OCH_3)-CHBr-CH_3, \end{array}$$

results on boiling monobromisosafrol dibromide,



$$C_6H_2Br\begin{array}{l} \diagup O \\ -O \end{array}\!\!>CH_2 \qquad \begin{array}{l} \\ \diagdown CHBr-CHBr-CH_3, \end{array}$$

with methyl alcohol. This compound separates from methyl alcohol in large, prismatic crystals, melting at 75° to 76.5°, and it was designated as the methyl alcohol addition-product of dibromisosafrol; it may perhaps be better termed α-methoxy-β-brom-dihydro-bromisosafrol. The analogous ethyl alcohol product was also described. It was likewise shown that corresponding methyl and ethyl alcohol products are formed in a similar manner from anethol dibromide, monobromanethol dibromide, isosafrol dibromide and ethyl isoeugenol dibromide. The alcohol products resulting from anethol and monobromanethol dibromides, isosafrol and ethyl isoeugenol dibromides, having the general formula,

$$R-CH(OR')-CHBr-CH_3,$$

were found to be readily converted by sodium methylate or alcoholic potash into ketones,

$$R-CO-CH_2-CH_3,$$

while the compounds obtained from monobromisosafrol dibromide are remarkably stable towards alkaline reagents, and they do not yield ketones on treatment with sodium alcoholate. The formation of the ketones from the first class of compounds is due to the elimination of the bromine atom in the β-position as hydrogen bromide, and the resulting unsaturated ether is then converted into a saturated ketone by hydrolysis and subsequent molecular rearrangement. In the second class of compounds, the β-bromine atom is not removed by the ordinary alkaline reagents.

Some months after the completion of the work described in the previous paper, Auwers and Müller[1] published an article on certain derivatives of the bromides of eugenol and isoeugenol. These

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[1] Auwers and Müller : *Ber. d. chem. Ges.*, **35**, 114.

chemists found that the bromine derivatives of eugenol, which may be represented by the general formula,

$$R—CH_2—CHBr—CH_2Br,$$

are not changed by the treatment with alcohols, aqueous acetone, sodium acetate, organic bases, etc., and that they show no abnormal reactions, but possess the character of ordinary phenols. On the other hand, however, the bromides of isoeugenol. having the formula,

$$R—CHBr—CHBr—CH_3.$$

are at once changed by cold methyl or ethyl alcohol, aqueous acetone and sodium acetate, one atom of bromine being eliminated and replaced by the corresponding radical. In every case the bromine atom which is removed is the one standing in the α-position to the benzene radical; the second or β-bromine atom does not enter into the reaction even at high temperatures or when the reagents, such as sodium acetate, are employed in a large excess. The formation of these compounds is represented by the formulas,

$$R—\underset{\alpha}{C}HBr—\underset{\beta}{C}HBr—CH_3 \rightarrow R—\underset{\alpha}{C}H(R')—\underset{\beta}{C}HBr—CH_3.$$

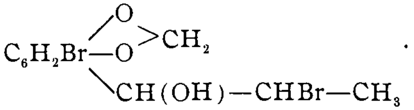
According to Auwers, therefore, the bromides of isoeugenol possess the character of pseudo-phenols, and in general the bromides of para-alkyl phenols, which contain bromine atoms in the α- and β-positions, react as pseudo-phenols.

A further point of considerable interest in Auwers's work is that when the ethers or alcohols, resulting by the treatment of isoeugenol dibromide or tribromide, are heated with alcoholic sodium methylate, the β-bromine atom is not eliminated as hydrogen bromide, as was found to be the case with the compounds derived from the bromides of isoeugenol ethers investigated in this laboratory, but it is replaced by the methoxyl-group; this reaction gives rise to ethers of glycols as is represented by the equation,

$$R—\underset{\alpha}{C}H(OCH_3)—\underset{\beta}{C}HBr—CH_3 + NaOCH_3 = NaBr + R—CH(OCH_3)—CH(OCH_3)—CH_3.$$

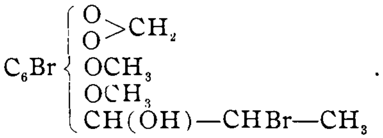
It will be readily seen from the foregoing that Auwers's work is more or less intimately related with the line of investigation which has been conducted in this laboratory for the past three years, the chief difference being that Auwers's researches were carried on with isoeugenol, a compound containing the free phenolic group, while our work is confined to the ethers of isoeugenol and of other propenyl phenols as anethol, isosafrol and isoapiol. This difference in the constitution of the compounds appears to exert a considerable influence upon the reactions of the substances derived from them, since in no case have we observed the formation of ethers of glycols as described by Auwers.

The experimental work described in this paper is a continuation of our investigations on the action of alcohols and aqueous acetone upon the bromides of isosafrol and isoapiol. From monobromisosafrol dibromide we have prepared a new alcohol,



$$C_6H_2Br\begin{cases}O \\ O\end{cases}\!\!>CH_2 \\ \quad\;\; CH(OH)—CHBr—CH_3 \quad .$$

its methyl and ethyl ethers, together with its acetyl and benzoyl derivatives; the same series of compounds is also obtained from monobromisoapiol dibromide, the new alcohol having the formula,

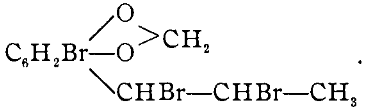


$$C_6Br\begin{cases}\begin{matrix}O \\ O\end{matrix}>CH_2 \\ OCH_3 \\ OCH_3 \\ CH(OH)—CHBr—CH_3\end{cases} \quad .$$

From this alcohol a new ketone has also been obtained.

EXPERIMENTAL.

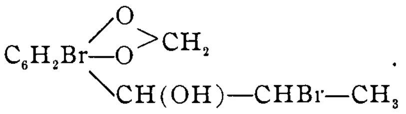
Monobromisosafrol Dibromide,[1]



$$C_6H_2Br\begin{cases}O \\ O\end{cases}\!\!>CH_2 \\ \quad\;\; CHBr—CHBr—CH_3 \quad .$$

This compound is readily prepared as previously described by treating an ethereal solution of isosafrol with two molecular proportions of bromine. It separates from a mixture of acetone and ether in colorless crystals, melting at 110° to 111°.

α-Oxy-β-brom-dihydro-bromisosafrol,



$$C_6H_2Br\begin{cases}O \\ O\end{cases}\!\!>CH_2 \\ \quad\;\; CH(OH)—CHBr—CH_3 \quad .$$

A solution of 10 grams of monobromisosafrol dibromide in 50 cc.

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[1] Pond, Erb and Ford: This Journal, **24**, 340.

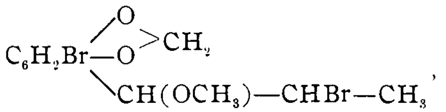
of acetone was heated to boiling and then treated with 15 cc. of water; the aqueous acetone solution was boiled in a reflux apparatus on the water-bath for two hours. The solution at first assumed a red color, which gradually became colorless. On completion of the reaction, the product was poured into an evaporating dish, and, after the evaporation of the acetone, a compound separated as a yellow-colored oil; after standing for about twelve hours, this oil solidified to a white, waxy substance, which was filtered, washed well with water and pressed on a porous plate. The crude compound is exceedingly soluble in alcohol and ether, hence it is best to crystallize first from acetone and to recrystallize from alcohol; it separates from these solvents in beautiful, large crystals, which melt at 89°.

Analysis gave the following results: Calculated for $C_{10}H_{10}O_3Br_2$, C. 35.50; H, 2.95; Br, 47.33. Found, C, 35.75, 35.78; H, 3.21, 3.07; Br, 47.23.

When this compound is boiled with alcoholic potash or sodium methylate, bromine is eliminated; on acidifying the reaction-product with hydrochloric acid and then adding water, an oil is formed. It was expected that this oil would exhibit the ordinary reactions of a ketone, but it failed to yield an oxime or semicarbazone, and its examination must be continued.

The methyl and ethyl ethers of the foregoing alcohol were described in a previous paper, but they will be briefly reviewed here for sake of completeness.

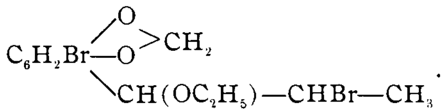
α-Methoxy-β-brom-dihydro-bromisosafrol,



$$C_6H_2Br\begin{cases}\begin{matrix}O \\ O\end{matrix}\Big>CH_2 \\ CH(OCH_3)—CHBr—CH_3\end{cases},$$

is formed when a solution of monobromisosafrol dibromide in methyl alcohol is boiled for a short time. It crystallizes from methyl alcohol in large prisms, melting at 75° to 76.5°.

α-Ethoxy-β-brom-dihydro-bromisosafrol,

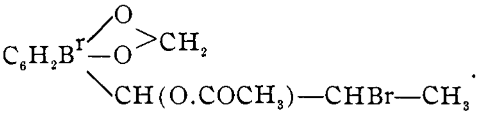


$$C_6H_2Br\begin{cases}\begin{matrix}O \\ O\end{matrix}\Big>CH_2 \\ CH(OC_2H_5)—CHBr—CH_3\end{cases}.$$

obtained by boiling a solution of isosafrol tribromide in ethyl alcohol, crystallizes from alcohol in large crystals, and melts at 58° to 60°.

Boiling, concentrated sodium alcoholate is without action upon these two ethers.

Acetate of α-Oxy-β-brom-dihydro-bromisosafrol,

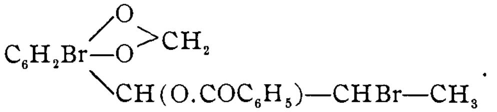


This compound is formed when a solution of 3 grams of potassium acetate in 5 cc. of glacial acetic acid is added to a solution of 10 grams of monobromisosafrol dibromide in 15 cc. of glacial acetic acid, and the whole is boiled for about five minutes.

The cold reaction-product is then poured into water; the compound separates as an oil, which solidifies after standing for about twelve hours. It is crystallized from alcohol, dried on a porous plate, and recrystallized from ethyl acetate; it separates from the latter solvent in fine, white needles, which melt at 73° to 74°.

Analysis gave the following results: Calculated for $C_{12}H_{12}O_4Br_2$, C, 37.89; H, 3.16. Found, C, 37.97, 37.63; H, 3.22, 3.26.

Benzoate of α-Oxy-β-brom-dihydro-bromisosafrol,

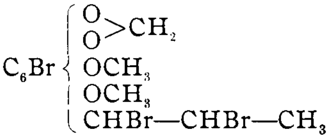


In order to prepare this benzoyl derivative of the alcohol, Einhorn and Hollandt's process was employed, since the ordinary Schotten-Baumann method employs alkali, which would lead to a decomposition of the alcohol.

Five grams of α-oxy-β-brom-dihydro-bromisosafrol were dissolved in 15 grams of pyridine, and 3 grams of benzoyl chloride were added slowly, with constant shaking; the mixture was allowed to stand during twenty-four hours, and then poured into dilute sulphuric acid (1 : 5). The benzoyl derivative separated at first as an oil, but solidified after repeated washing with dilute acid and water, and was crystallized from a mixture of ether and acetone; it forms long, white crystals, melting at 142° to 143°. It is readily soluble in the usual solvents.

Analysis gave the following results: Calculated for $C_{17}H_{14}O_4Br_2$, C, 46.15; H, 3.16. Found, C. 46.27, 46.10; H. 3.24, 3.21.

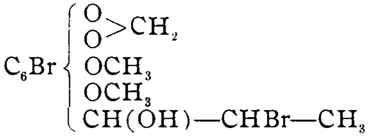
Monobromisoapiol Dibromide,



$$C_6Br\begin{cases} \begin{matrix}O\\O\end{matrix}>CH_2 \\ OCH_3 \\ OCH_3 \\ CHBr{-}CHBr{-}CH_3 \end{cases}$$

prepared as previously described[1] by the action of two molecular proportions of bromine upon an ethereal solution of isoapiol, crystallizes from acetone and melts at 120°.

α-Oxy-β-brom-dihydro-bromisoapiol,



$$C_6Br\begin{cases} \begin{matrix}O\\O\end{matrix}>CH_2 \\ OCH_3 \\ OCH_3 \\ CH(OH){-}CHBr{-}CH_3 \end{cases}$$

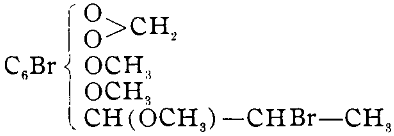
Twenty grams of monobromisoapiol dibromide were dissolved in 100 cc. of acetone and treated with 30 cc. of water; after boiling for two hours in a reflux apparatus, the acetone was allowed to evaporate and the oily residue was washed well with water. The oil gradually solidified, was washed, dried, and crystallized from alcohol; it separated in large, well-defined crystals, melting at 85° to 86°.

The compound is readily soluble in the usual solvents. When boiled with alcoholic potash, one atom of bromine is removed and a new compound is formed, which will be subsequently described.

Analysis gave the figures: Calculated for $C_{12}H_{14}O_5Br_2$, C, 36.18; H, 3.52; Br, 40.20. Found, C. 36.21, 35.98; H. 3.61, 3.31; Br, 40.34.

The methyl and ethyl ethers of the above-mentioned alcohol are easily obtained by boiling a solution of isoapiol tribromide in methyl or ethyl alcohol.

α-Methoxy-β-brom-dihydro-bromisoapiol,



$$C_6Br\begin{cases} \begin{matrix}O\\O\end{matrix}>CH_2 \\ OCH_3 \\ OCH_3 \\ CH(OCH_3){-}CHBr{-}CH_3 \end{cases}$$

A solution of 20 grams of monobromisoapiol dibromide in 50 cc.

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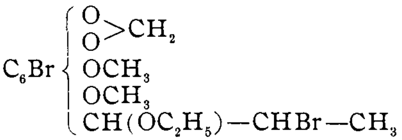
[1] See Pond, Erb and Ford: This Journal, **24**, 343.

of methyl alcohol is boiled for a few minutes and then poured into a crystallizing dish; the compound separates in large crystals, which melt at 92° to 93°.

Analysis gave: Calculated for $C_{13}H_{16}O_5Br_2$, C, 37.86; H, 3.88; Br, 38.83. Found, C, 38.02, 38.01; H, 3.90, 3.99; Br, 38.78, 38.85.

α-Ethoxy-β-brom-dihydro-bromisoapiol,



$$C_6Br\left\{\begin{array}{l}\begin{matrix}O\\O\end{matrix}>CH_2\\OCH_3\\OCH_3\\CH(OC_2H_5)-CHBr-CH_3\end{array}\right.$$

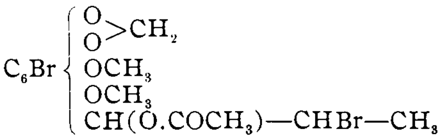
Twenty-eight grams of monobromisoapiol dibromide were dissolved in ethyl alcohol, and the solution was boiled for ten minutes; on cooling, this compound separated in large crystals, melting at 72° to 73°.

In our previous communication, this compound was described as an oil, and at that time it was impossible to induce the substance to solidify; now, however, we find no difficulty in obtaining a crystalline product at once. We are unable to find a satisfactory explanation for this difference in the behavior of the substance, unless we attribute it to a slightly purer isoapiol tribromide.

The compound was analyzed with the following results: Calculated for $C_{14}H_{18}O_5Br_2$, C, 39.43; H, 4.22. Found, C, 39.59, 39.20; H, 4.00, 4.05.

Hot, concentrated solutions of alcoholic potash and sodium methylate are without action upon these ethers.

Acetate of α-Oxy-β-brom-dihydro-bromisoapiol,



$$C_6Br\left\{\begin{array}{l}\begin{matrix}O\\O\end{matrix}>CH_2\\OCH_3\\OCH_3\\CH(O.COCH_3)-CHBr-CH_3\end{array}\right.$$

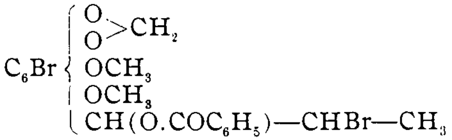
A hot solution of 2.5 grams of potassium acetate in 5 cc. of glacial acetic acid was added slowly, and with shaking, to a warm solution of 10 grams of monobromisoapiol dibromide in 15 cc. of glacial acetic acid, and the mixture was brought to a boiling temperature.

The cold reaction-product was then poured into water, extracted with ether, and the ethereal solution washed with water, dried over calcium chloride, filtered and the ether allowed to evaporate.

The substance remained as an oil, which solidified slowly; it was crystallized from ether and melted at 114° to 115°.

Analysis for carbon and hydrogen gave: Calculated for $C_{14}H_{16}O_6Br$, C, 38.18; **H**, 3.63. Found, C, 37.89, 38.18; H, 3.90, 3.58.

Benzoate of α-Oxy-β-brom-dihydro-bromisoapiol,



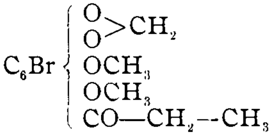
$$C_6Br\left\{\begin{array}{l} \begin{array}{l}O\\O\end{array}\!>CH_2 \\ OCH_3 \\ OCH_3 \\ CH(O.COC_6H_5)—CHBr—CH_3 \end{array}\right.$$

This ester was obtained according to the Einhorn-Hollandt method of preparing benzoyl derivatives.

Five grams of α-oxy-β-brom-dihydro-bromisoapiol were dissolved in 15 cc. of pyridine and treated with 3 grams of benzoyl chloride, which was added gradually. After standing during twenty-four hours, the reaction-mixture was poured into dilute sulphuric acid (1:5), and allowed to remain until the oil, which at first separated, had solidified; the solid was then filtered, washed with dilute acid and water, and crystallized from alcohol. It separates in well-defined crystals, which melt at 117° to 118°.

The following figures were obtained by analysis: Calculated for $C_{19}H_{18}O_6Br_2$, C, 45.41; H, 3.58. Found, C, 45.14, 45.13; H, 3.64, 3.44.

α-Keto-dihydro-bromisoapiol,



$$C_6Br\left\{\begin{array}{l} \begin{array}{l}O\\O\end{array}\!>CH_2 \\ OCH_3 \\ OCH_3 \\ CO—CH_2—CH_3 \end{array}\right.$$

Although the ethers of α-oxy-β-brom-dihydro-bromisoapiol are not affected by boiling with concentrated solutions of alcoholic potash or sodium methylate but, in fact, separate from these solutions on cooling and show their original melting-points, nevertheless the free alcohol itself is quite readily changed by the action of hot alcoholic potash. A similar circumstance was noted in the behavior of the derivatives from isosafrol as described above. The compound obtained from the α-oxy-isosafrol derivative is an oil, while that formed from the α-oxy-isoapiol derivative is a crystalline substance, and analysis seems to indicate that it is a ketone.

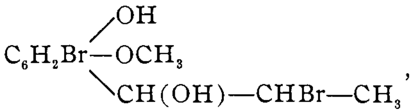
Five grams of α-oxy-β-brom-dihydro-bromisoapiol (m. p. 85° to 86°) were dissolved in 25 cc. of ethyl alcohol, treated with a concentrated solution of 2 grams of potassium hydroxide in alcohol, and boiled in a reflux apparatus for about two hours; at the expiration of this time the separation of potassium bromide was complete and 100 cc. of water were added. Five cc. of hydrochloric acid were then introduced, and the whole boiled for about half an hour. After standing for about twelve hours, a solid substance separated; this was filtered, dried, and crystallized from alcohol. It melts at 128° to 129°.

Another preparation of this substance was made by boiling 23 grams of the α-oxy-compound with a solution of 7 grams of potassium hydroxide in 100 cc. of alcohol, and subsequently treating with water and acid as above-mentioned. The solid product crystallized from alcohol in beautiful, small crystals, which melt at 128° to 129° and are rather sparingly soluble in alcohol.

Analysis gave the following results: Calculated for $C_{12}H_{13}O_5Br$, C, 45.42; H, 4.10. Found, C, 45.36, 45.67; H, 4.45, 4.31.

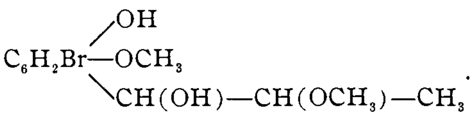
The analysis, therefore, indicates the formula given above. That this compound is a ketone, however, has not been absolutely proved, since our investigation was interrupted at this point; we expect to continue it during the current year. It is exceedingly probable that the substance will prove to be the ketone.

According to Auwers and Müller,[1] α-oxy-β-brom-monobrom-dihydro-isoeugenol,



$$\mathrm{C_6H_2Br}\begin{array}{l}\diagup \mathrm{OH}\\ -\mathrm{OCH_3}\\ \diagdown \mathrm{CH(OH)-CHBr-CH_3}\end{array},$$

obtained by the action of aqueous acetone upon monobromisoeugenol dibromide, reacts with sodium methylate, yielding α-oxy-β-methoxy-monobrom-dihydro-isoeugenol,



$$\mathrm{C_6H_2Br}\begin{array}{l}\diagup \mathrm{OH}\\ -\mathrm{OCH_3}\\ \diagdown \mathrm{CH(OH)-CH(OCH_3)-CH_3}\end{array}.$$

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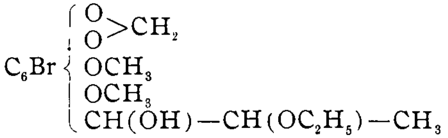
[1] Auwers and Müller : *Ber. d. chem. Ges.*, **35**. 121.

If a similar reaction had taken place in the treatment of α-β-oxy-brom-dihydro-brom-isoapiol with ethyl alcoholic potash, a compound having the following composition would have resulted:



$$C_6Br\left\{\begin{array}{l} \begin{matrix}O\\O\end{matrix}>CH_2 \\ OCH_3 \\ OCH_3 \\ CH(OH)-CH(OC_2H_5)-CH_3 \end{array}\right.$$

This substance contains 46.28 per cent. of carbon and 5.23 per cent. of hydrogen, which are quite different from the figures obtained by analysis. For the present, therefore, we prefer to retain the ketone formula above-mentioned. This line of investigation will be continued and extended to some other substances of a similar constitution.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE NO. 47.—SENT BY H. W. WILEY.]

THE COMPOSITION OF FRESH AND CANNED PINEAPPLES.

BY L. S. MUNSON AND L. M. TOLMAN.

Received January 2, 1903.

THE work undertaken in connection with the investigation of the composition of fresh and canned pineapples consists of the analysis of (1) fresh pineapples from various sources, (2) canned pineapples that were put up under supervision of the Consuls General of the United States at Singapore and Nassau, and (3) commercial samples of canned pineapples.

DESCRIPTION OF SAMPLES.

Of the thirty-eight samples of fresh pineapples examined, twenty-one were from Florida, ten from Cuba, four from Porto Rico, two from the Bahamas and one from Jamaica. The Florida pineapples were largely obtained from representative growers; the Cuban pineapples were nearly all purchased on the market at Havana; the Porto Rican pineapples were obtained from F. D. Gardner, Director of Porto Rican Experiment Station; the Bahama samples were obtained on the market in New York; and the sample from Jamaica was obtained in the Washington market. So far as possible, the samples obtained were the well-ripened fruit. but in some cases they were shipped so far that it was not