**Oleic Acid.**—Although we were able to free ethyl gorlate from ethyl oleate by fractional distillation we were not able to free the ethyl oleate from the ethyl gorlate. The elaidic acid test is not satisfactory in the presence of gorlic acid as the latter gives a similar reaction. However, oxidation by permanganate yielded dihydroxystearic acid. The presence of oleic acid was confirmed further by the boiling point of the acid and of ethyl oleate and by the correct iodine numbers for mixtures with gorlic acid or ester. The oxidation products of hydnocarpic, chaulmoogric and gorlic acids (hydroxy and keto acids) were present only in very small amounts and were not isolated.

### Quantitative Analysis

The total fatty acids of the oil, when separated into liquid and solid acids by the method outlined above, consisted of 74.8% solid and 25.2% liquid acids. The separation of course is not complete, but the solid fraction should contain not over 1 or 2% of liquid acids. From the qualitative analysis it is seen that the solid fraction consists essentially of palmitic, hydnocarpic and chaulmoogric acids. The distillation curve (Fig. 1) shows that a sharp separation of chaulmoograte is obtained. If 100 cc. of esters is distilled, the percentage of ethyl chaulmoograte in any fraction (boiling point above 200°) is computed easily from the specific rotation of the fraction, *i. e.*, Fraction No. 6, Table II, (53.54/55.4) × 100 = 96.6%. 96.6 × 23 = 22.2 cc. of ethyl chaulmoograte.

Total % of ethyl chaulmoograte in esters from solid acids = 30.8. 30.8 × 0.748 = 23.1% chaulmoogric acid in solid fraction of F. F. A. The same procedure is used with fractions boiling below 201° to obtain the percentage of hydnocarpic acid, the palmitic being obtained by difference.

The method of computing the percentage composition of the liquid acids in fractions 5, 6 and 7, Table III, is as follows: the percentage of optically inactive acid may be computed by using 55.5° as the specific rotation of both ethyl gorlate and chaulmoograte, *i. e.*, in Fraction 5, (44.03/55.5) × 100 = 79.4%. 100 − 79.4 = 20.6% ethyl oleate. 20.6% of 23.5 cc. = 4.8 cc. oleate. Then if $x = 82$ (iodine no. of both oleate and chaulmoograte) and if $y = 167$ (iodine no. of gorlate), the percentages of gorlate and chaulmoograte can be calculated from the formulas, $x + y = 100$ and $\frac{82x}{100} + \frac{167y}{100} =$ I no. (of fraction). In fraction 4 the specific rotation and iodine number indicated that only gorlate and oleate were present. In fractions 1, 2 and 3, palmitate was obtained by difference after the other esters present had been computed.

TABLE IV

PERCENTAGE COMPOSITION OF THE FATTY ACIDS OF *C. brasiliensis* OIL (FROM TABLES II AND III AND ACCORDING TO PAGET)

| Fatty acid | Composition according to Cole, % | Paget, % |
|---|---|---|
| Hydnocarpic acid | 45.0 | 65–70 |
| Chaulmoogric acid | 24.4 | |
| Palmitic acid | 6.6 | |
| Gorlic or dehydrochaulmoogric | 15.4 | 9 |
| Oleic acid | 6.3 | 4 |
| Keto acids | . . | 4 |
| "Tarry acids" | None | 9 |
| Residue (decomposition products of distillation) | 2.3 | . . |

## Summary

A method for the qualitative and quantitative analysis of chaulmoogra oils is described.

The analysis of the fatty acids of *C. brasiliensis* oil as made by this method is given.

RIO DE JANEIRO, BRAZIL RECEIVED JANUARY 8, 1938

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[CONTRIBUTION FROM THE INTERNATIONAL LEPROSY CENTER, RIO DE JANEIRO]

# Analysis of Chaulmoogra Oils. II. *Oncoba echinata* (Gorli) Oil

BY HOWARD IRVING COLE AND HUMBERTO T. CARDOSO

*Oncoba echinata*, Oliver, a tall shrub, from the seeds of which oil of gorli or *beurre de gorli* is obtained, is indigenous to West Africa. Gorli oil has been used in the treatment of leprosy. It is solid at ordinary temperatures and resembles that of *Hydnocarpus alcalae* in having a high melting point and in containing chaulmoogric but not hydnocarpic glycerides. Owing to the difficulty of separating these two compounds, the absence of the latter makes this oil a good source of pure chaulmoogric acid. In fact, until recently, the only correct figures for the constants of chaulmoogric acid have been obtained from this oil. The absence of hydnocarpic acid also so simplifies the analysis that oils of this type are the only chaulmoogra oils for which definite quantitative results have been published. Even so, the analyses have been only approximate.

The first analysis of the oil of gorli was made by Goulding and Akers(1) in 1913. They stated that the fatty acids consisted of 85.5% chaulmoogric acid and 12.5% liquid acids. André and Jouatte(2) in 1928 found that the liquid acid fraction contained an optically active liquid fatty acid with a

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(1) Goulding and Akers, *Proc. Chem. Soc.* (London), **29**, 197 (1913).

(2) André and Jouatte, *Bull. soc. chim.* **43**, 347 (1928).

high iodine number. They named it gorlic acid. The structure of this acid recently was worked out by Paget[3] who called it dehydrochaulmoogric acid. He obtained it from *Carpotroche brasiliensis* oil and did not correlate it with gorlic acid from oil of gorli. Lately we have shown that these two acids are identical and have been able to purify the acid and determine its constants.[4] André stated that the fatty acids of oil of gorli contained about 10% palmitic acid, 10–12% gorlic acid and the remainder chaulmoogric acid.

We have analyzed oil of gorli by the method for chaulmoogra oils recently described.[5] Our analysis is shown in Table I.

TABLE I

PERCENTAGE COMPOSITION OF THE FATTY ACIDS OF (*Oncoba echinata* (GORLI) OIL (FROM TABLES II AND III)

| Acid | Per cent. |
|---|---|
| Palmitic | 7.8 |
| Oleic | 2.2 |
| Gorlic | 14.7 |
| Chaulmoogric | 74.9 |
| Loss | 0.4 |

## Experimental

The sample of gorli oil was obtained through the kindness of the French Ministry of Colonies and Dr. Tisseuil, Director of the Central Institute of Leprosy, French West Africa. The oil was extracted from the crushed seeds of the 1936 crop by boiling with water, allowing the fat to rise and then cooling. The solidified oil was separated from water and filtered while hot. The constants of the sample were determined at the same time that the analysis was made and are as follows: iodine no. (Hanus), 96.4; saponification no., 193.7; F. F. A. (as oleic), 4.3; specific optical rotation $[\alpha]^{25}\text{D}$ +51.70°.

**Method of Analysis.**—The oil was saponified and the fatty acids liberated and washed in the usual manner. The solid acids were separated from the liquid acids by crystallization from 80% ethyl alcohol. The two fractions were made into ethyl esters and then were fractionally distilled in a Podbielniak Model B high temperature fractionating apparatus. The details of the separation and distillation were given in the first article of this series.[5]

**Qualitative Analysis.**—The fatty acids of gorli oil contain palmitic, oleic, gorlic and chaulmoogric acids. They were isolated and identified as follows.

**Palmitic Acid.**—This acid was isolated from the first fraction in both the runs given in Tables II and III. The method used was that previously described.[5] Correct boiling and melting points were obtained for both the ethyl palmitate and palmitic acid.

**Oleic Acid.**—The presence of oleic acid was indicated in the liquid acid fraction by the distillation curve of the ethyl esters. Its presence was proved by obtaining dihydroxystearic acid upon oxidizing fractions 2 and 3, Table III, with permanganate. The elaidic acid test could not be used as gorlic acid gives a similar reaction.

TABLE II

FRACTIONAL DISTILLATION OF ETHYL ESTERS FROM SOLID FATTY ACIDS OF GORLI OIL (79.2% OF TOTAL FATTY ACIDS)

| Fr. | B. p., °C. (10 mm.) | Cc. | Sp. rot. $[\alpha]^{25}\text{D}$ | Iodine no. | Palmitate, cc. | Oleate, cc. | Gorlate, cc. | Chaulmoograte, cc. |
|---|---|---|---|---|---|---|---|---|
| 1 | 190–200 | 6.6 | 5.85 | 11.27 | 5.73 | 0.17 | 0.04 | 0.66 |
| 2 | 200–214 | 4.4 | 29.46 | 40.80 | 2.08 | .. | .. | 2.32 |
| 3 | 214–221 | 89.0 | 54.5 | 82.09 | .. | .. | .. | 89.00 |
| % in solid fraction | | | | | 7.81 | 0.17 | 0.04 | 91.98 |
| % in total fatty acids | | | | | 6.19 | 0.13 | 0.03 | 72.85 |

TABLE III

FRACTIONAL DISTILLATION OF ETHYL ESTERS FROM LIQUID FATTY ACIDS OF GORLI OIL (20.8% OF TOTAL FATTY ACIDS)

| Fr. | B. p., °C. (10 mm.) | Cc. | Sp. rot. $[\alpha]^{25}\text{D}$ | Iodine no. | Palmitate, cc. | Oleate, cc. | Gorlate, cc. | Chaulmoograte, cc. |
|---|---|---|---|---|---|---|---|---|
| 1 | 192–209 | 6.6 | 27.68 | 75.87 | 3.3 | ... | 2.7 | 0.6 |
| 2 | 209–213 | 10.9 | 45.33 | 141.9 | ... | 2.0 | 7.7 | 1.2 |
| 3 | 213–215 | 21.0 | 49.96 | 151.7 | ... | 2.0 | 17.2 | 1.7 |
| 4 | 215 | 3.6 | 52.85 | 147.7 | ... | 0.2 | 2.8 | 0.7 |
| Residue | | 0.9 | | | | | | |
| Total cc. | | 43.0 | | | 3.3 | 4.2 | 30.4 | 4.2 |
| % in total fatty acids cc. × (20.8/43) | | | | | 1.60 | 2.03 | 14.71 | 2.03 |
| % residue in total fatty acids, 0.43 | | | | | | | | |

**Gorlic Acid.**—Gorlic acid was isolated from fractions rich in this acid such as fraction 3, Table III, by the method previously described[5] and the correct constants obtained for ethyl gorlate and gorlic acid.[4]

**Chaulmoogric Acid.**—Fraction 3, Table II, was nearly pure ethyl chaulmoograte. After changing it to acid and crystallizing twice from 80% ethyl alcohol, pure chaulmoogric acid was obtained with the correct optical rotation, iodine, number, neutralization equivalent and melting point.

**Quantitative Analysis.**—The total fatty acids of gorli oil when separated into liquid and solid acids by our method consisted of 79.2% solid acids and 20.8% liquid acids. The separation is not complete as can be seen from Tables II and III. The solid fraction contains only 0.21% of liquid acids while the liquid acid fraction still contains 17.4% of solid acids in solution. Separation by crystallization from 80% acetone yielded even less satisfactory results. A complete separation is not necessary, however, as the amounts of the various constituents can be computed by taking advantage of the boiling points, optical activity, and iodine numbers or the absence of one or both of the two latter constants as described in Part I of this series. The results of these computations are given in Tables II and III and these are summarized in Table I. The percentage composition as given should be accurate within 1 or 2%. As a check on our method, the specific optical rotation of the total fatty acids was determined and compared with the rotation calculated from the percentages of gorlic and chaulmoogric acids given in Table I; found for total fatty acids, +54.16°; calcd. 54.08°. This very close check is more apparent than real as the loss of 0.4% is

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[3] Paget, *J. Chem. Soc.*, 955 (1937).

[4] Cole and Cardoso, THIS JOURNAL, **60**, 612 (1938).

[5] Cole and Cardoso, *ibid.*, **60**, 614 (1938).

probably chiefly gorlic acid. Assuming this to be the case, the calculated result would be +54.32°, which is still in very close agreement with the actual value.

## Summary

The qualitative and quantitative analysis of the fatty acids of *Oncoba echinata* (gorli) oil has been made by the methods given in the first article of this series. The percentage composition of the fatty acid is as follows: palmitic acid, 7.8%, oleic acid, 2.2%, gorlic acid, 14.7% and chaulmoogric acid, 74.9% (loss, 0.4%).

RIO DE JANEIRO, BRAZIL RECEIVED JANUARY 8, 1938

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

# The Reactions between Mercury Diaryls and Selenium Tetrabromide

BY HENRY M. LEICESTER

Since mercury diaryls have been shown to react readily with diaryl selenium dihalides[1] it seemed desirable to test the action of the mercury compounds on simpler selenium derivatives such as selenium tetrabromide. In the course of this work, a new method for the synthesis of aromatic selenides was developed.

When mercury diaryls were added to a solution of selenium tetrabromide in carbon bisulfide, it was found that three molar equivalents of the mercury compound were required to discharge the red color from one molar equivalent of the tetrabromide. The reaction was rapid and a heavy precipitate of aryl mercuric bromide settled out almost quantitatively. From the solution were isolated aryl bromides and diaryl selenides. Thus, the reaction was entirely analogous to that found with diaryl selenium dibromides, and was represented by the equation

$$SeBr_4 + 3R_2Hg = R_2Se + RBr + 3RHgBr \quad (1)$$

It is clear that this reaction gives a very rapid and easy method for synthesizing diaryl selenides. Such a synthesis is especially important in the case of compounds containing heavy organic radicals, such as naphthyl or biphenyl. When attempts were made to synthesize these selenides by the diazo reaction[2] the chief products were tars from which the selenides could not be isolated in a pure condition. In this new reaction, they were readily obtained pure.

It was found that when an excess of selenium tetrabromide was present in reaction (1), mercuric bromide was also formed. Aryl mercuric bromides reacted with selenium tetrabromide to give the same salt. The other products formed were again aryl bromides and diaryl selenides. Thus, the second reaction was

$$SeBr_4 + 3RHgBr = R_2Se + RBr + 3HgBr_2 \quad (2)$$

Therefore, the total reaction which can be obtained with an excess of the tetrabromide is

$$2SeBr_4 + 3R_2Hg = 3HgBr_2 + 2R_2Se + 2RBr$$

## Experimental

Selenium tetrabromide was prepared by adding excess bromine to gray, powdered selenium and driving off the unreacted bromine by gentle warming.

When dry mercury diphenyl and selenium tetrabromide were mixed, a reaction of almost explosive violence occurred. Therefore, the reaction always was carried out in carbon bisulfide, in which all the reagents were at least partly soluble. When three moles of mercury diphenyl was added with shaking to one mole of selenium tetrabromide in carbon bisulfide, heat was evolved and the red color faded rapidly as a heavy white precipitate came down. Mercury di-*p*-tolyl reacted in a similar way. When mercury di-β-naphthyl and mercury dibiphenyl were used, the reaction was much more sluggish, and the mixtures were warmed gently on the water-bath and stirred during the addition of the mercury compound. The precipitate was filtered off, and in all cases was identified as the aryl mercuric bromide by m. p. and mixed m. p. with authentic specimens. The yields were as follows: phenylmercuric bromide 95%, *p*-tolylmercuric bromide 82%, β-naphthylmercuric bromide 87% and biphenylmercuric bromide 100%. In one case, one mole of selenium tetrabromide was treated with four of mercury diphenyl, but the yield of phenylmercuric bromide was not increased. It thus appears that the reaction is practically quantitative in the sense of equation (1) above, and the failure to obtain 100% yields in all cases was probably due to the difficulty in handling the small amounts of material used.

After separation of the aryl mercuric bromides, the carbon bisulfide solutions were evaporated to dryness. Phenyl and *p*-tolyl selenides and bromides were separated by fractionation. In the case of the naphthyl and biphenyl compounds, the residue was taken up in alcohol, and the selenide was crystallized from this solvent. Careful addition of water to the mother liquors from the crystallizations at first precipitated a small amount of selenide and then, suddenly, the bromide. In view of the difficulty of quantitative isolation of these compounds,

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[1] Leicester, THIS JOURNAL, **57**, 1901 (1935).

[2] Leicester and Bergstrom, *ibid.*, **53**, 4428 (1931).