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Effects of Irradiation of Crude Coal Tar by Quartz Mercury Vapor Lamps. I. Evidence of chemical changes as shown by changes in absorption spectra.

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The stimulus to investigations on the possible changes in the absorption of crude coal tar when irradiated by air-cooled quartz mercury vapor lamps was furnished by the fact that a simple but apparently beneficial treatment for psoriasis consists in irradiating, with sources rich in ultraviolet light, affected areas which are covered with a thin film of crude coal tar ointment.[1] Neither the ointment nor irradiation alone produces as marked results; hence the combination of the 2 is used simultaneously. The so-called crude coal tar ointment is made up of 2 drams each of crude coal tar and pulverized zinc oxide mixed with 2 ounces each of corn starch and petrolatum.

It seemed highly probable that the only substance in this ointment which might give evidence of chemical change under ultraviolet irradiation was the crude coal tar and that, by investigations of a spectroscopic character, it might be possible to determine which portion of the crude coal tar was the active or stimulating agent. Thus far we have settled definitely only the question relative to changes in absorption spectra produced by irradiation with an air-cooled quartz mercury vapor lamp. The lamp used was made by the Victor X-Ray Corporation and was operated at 90 volts at a distance of 17 cm.

The apparatus for obtaining absorption spectra is shown in Fig. 1. A 0.5 kilowatt transformer is used for electrical excitation together with a suitable condenser which is joined in parallel (multiple) with a spark-gap consisting of one electrode of aluminum and one of nickel separated by a few millimeters. The photographic plates used for obtaining the spectrograms were made more sensitive to the extreme ultraviolet irradiation by treatment with oil. In the development of the plate the oil is carefully removed with anhydrous ether before it is immersed in the developer. Of the various possible solvents for crude coal tar, ether was chosen because it is least opaque to the ultraviolet region and does not change appreciably (if at all) when exposed to prolonged irradiation. Toluol, benzene,

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[1] Goeckerman, W. H., *Northwest Med.*, 1925, xxiv, 229.

xylol and carbon tetrachloride were discarded because they were too opaque when used with the particular depth of quartz cell (1.346 mm.) employed in these investigations. Chloroform is an excellent solvent for crude coal tar but cannot be used because of the chemical action produced by prolonged irradiation.

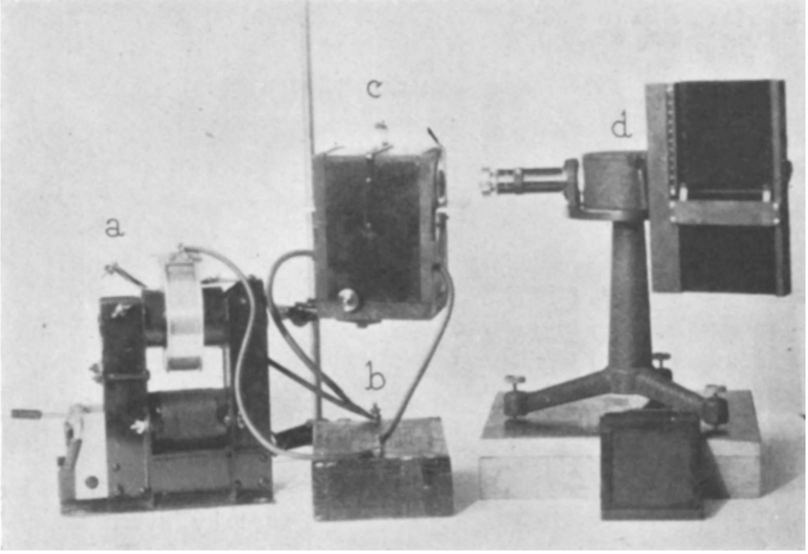

FIG. 1.
Ensemble of apparatus for producing a spark discharge in air and for photographing the spectra in both the visible and the ultraviolet regions: *a*, transformer; *b*, condenser; *c*, spark-gap; *d*, quartz spectrograph.

Spectral changes produced by irradiation of solutions (ether) of crude coal tar. A saturated ether solution of crude coal tar was made and this was diluted by putting 1 cc. of it in 1000 cc. of ether. The diluted solution was put in the quartz cell and carefully sealed. Absorption spectra were taken before and after irradiation. Fig. 2 shows the changes in absorption spectra due to irradiation. Fig. 3 shows the increased spectral absorption of a freshly diluted solution of crude coal tar after standing for periods varying from 20 minutes to 24 hours. Fig. 4 demonstrates that the 24 hour old solution can again be made more transmissive spectrally after successive periods of irradiation. From these and similar spectrograms it is found that the effect of ageing is to increase the absorption. These ageing solutions, however, may be made more transmissive by subsequent ultraviolet irradiation, but the limits and percentages of transmission do not equal those possessed by the original, freshly prepared solution.

Spectral changes produced by the irradiation of crude coal tar (thin film method). In order to avoid any action caused by the presence of a solvent, a thin-film method was employed. Thin films were made by allowing a drop of a 5% benzene solution to fall on a quartz plate.* On the evaporation of the benzene a film of crude coal tar remained, frequently of the order of thickness of 1000 molecules.[2] This film was covered by a second quartz plate and a region of apparently uniform thickness and character care-

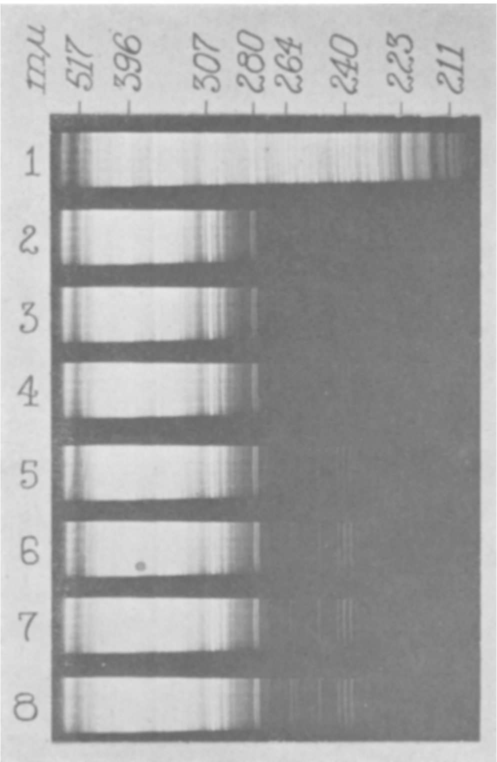

FIG. 2.

1. Spark (air) between electrodes. 2. Quartz cell filled with ether solution of crude coal tar and interposed between the spark-gap and the slit of the spectrograph. 3. Same, 15 minutes later. 4. Same, after a 15 minute irradiation. 5. Same, after an additional 30 minute irradiation. 6. Same, after an additional 60 minute irradiation. 7. Same, after an additional 60 minute irradiation. 8. Same, after an additional 60 minute irradiation. Times of exposure: (1), 20 seconds; (2-8), 60 seconds.

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* We desire to acknowledge the assistance of Professor Anthony Zeleny and Professor Charles A. Mann of the University of Minnesota in matters pertaining to the technic of the preparation of thin films.

[2] Harkins, W. D., and Feldman, Aaron, *J. Am. Chem. Soc.*, 1922, xliv, 2665.

fully marked off. This enabled us to take successive photographs of the absorption spectra in the same region of the film, so that errors due to nonuniformity of film were obviated. This method presents many difficulties in technic and it is practically impossible to obtain 2 films exactly alike.

Fig. 5 shows a true effect due to irradiation over and above any changes that may occur as the result of ageing. Differences between spectrograms 4 and 5 are due to changes other than irradiation in an interval of 41 hours. Differences between spectrograms 5 and 7 are due to an irradiation of 165 minutes. Spectrograms 5 and 7 were taken immediately after irradiation, so that any changes due to ageing are reduced. Since the differences between spectrograms 5 and 7 are much more marked than those between 4 and 5 and since there is a time interval of only 165 minutes between 5 and 7,

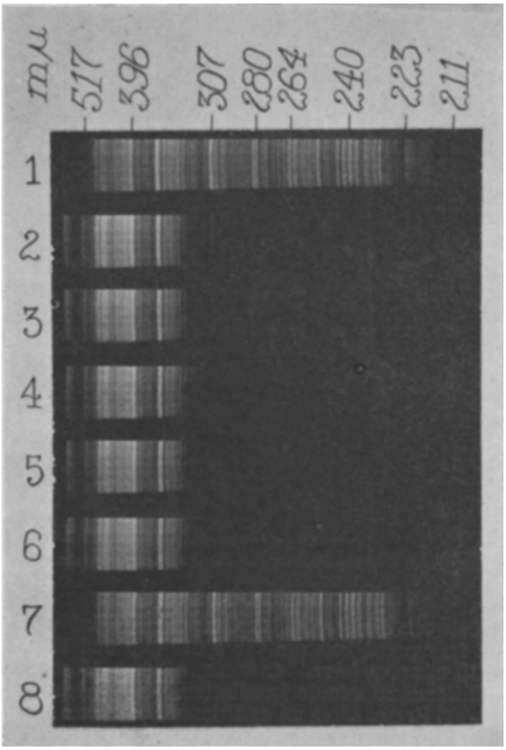

FIG. 3.
1. Spark spectrum. 2. Ether solution of crude coal tar. 3. Same, after 20 minutes. 4. Same, after additional interval of 35 minutes. 5. Same, after additional interval of 60 minutes. 6. Same data as for 5. 7. Spark spectrum. 8. Ether solution following morning (total interval, 24 hours). Times of exposures: (1 to 7), 20 seconds; remainder, 60 seconds.

whereas there is a time interval of 41 hours between 4 and 5, the change is undoubtedly due to the ultraviolet irradiation.

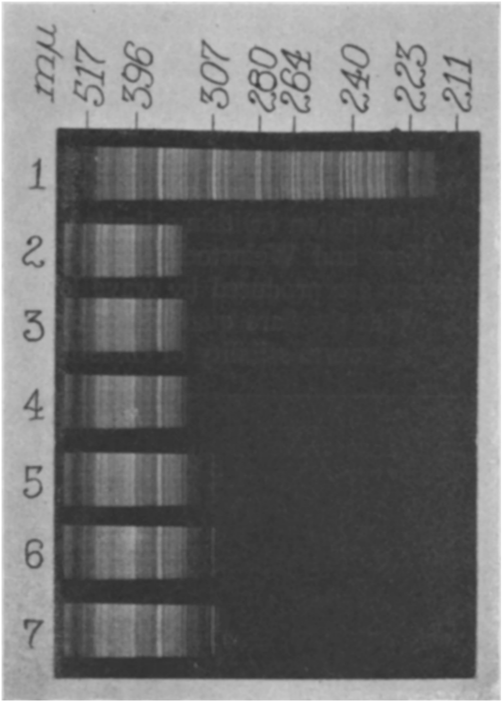

FIG. 4.

1. Spark spectrum. 2. Same as No. 8 in Fig. 3. 3. Same, after 15 minute irradiation. 4. Same, after additional 30 minute irradiation. 5. Same after additional 60 minute irradiation. 6. Same, after additional 60 minute irradiation. 7. Same, after additional 45 minute irradiation. Times of exposures: (1), 20 seconds; (2-7), 60 seconds.

Fig. 6 shows changes in the absorption spectra of a film of crude coal tar (made by the deposition method) both with and without irradiation. There are changes due to ageing. These changes are, however, much less marked than those due to irradiation. The thinner the film the more marked these ageing effects seem to be. Films of crude coal tar, made after the manner of blood smears, were irradiated and then dissolved in ether. These solutions also showed an increased transmission of ultraviolet light produced by irradiation. During irradiation of the crude coal tar, whether in thin films or in solution, special precaution was taken to avoid changes due to heating effects. The substance to be irradiated was placed in an open petri dish on finely chopped ice and a heat-wave filter (consisting of a column of 2 inches of water in contact with a plate of transparent fused quartz) was interposed between the mercury quartz lamp and the dish containing the solution. In all instances the absorption spectra were photographed immediately following irradiation.

It is of interest to compare the results of our investigations with those of Hess and Weinstock[3] on changes in spectral transmission of cholesterol when irradiated by quartz mercury vapor lamps. In many particulars the phenomena observed are the same. The irradiated cholesterol absorbed ultraviolet radiations to a less degree than ordinary cholesterol: an effect which is intensified with increasing degrees of irradiation (within a limited time). By means of suitable filters Hess and Weinstock showed that little if any changes on irradiation are produced by wave lengths longer than 302 millimicrons. With the bare quartz mercury lamps and with sufficient exposure the transmissibility of cholesterol is increased to

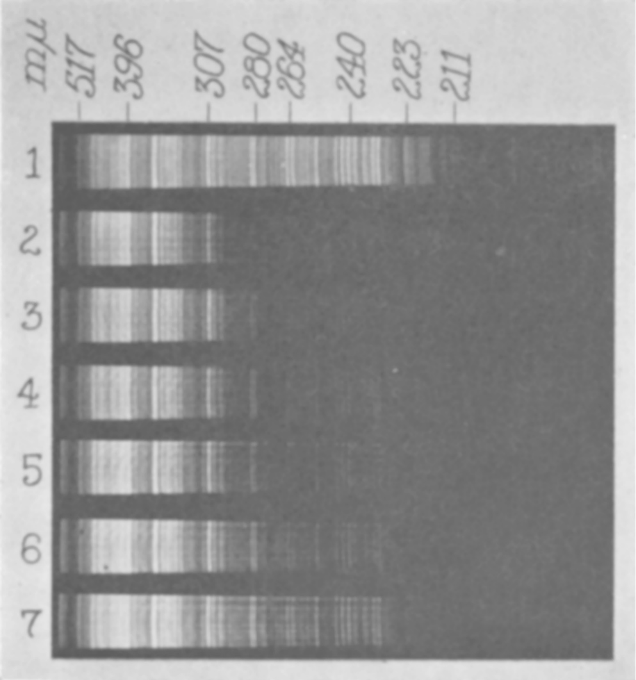

FIG. 5.

1. Spark spectrum. 2. Non-irradiated film of crude coal tar between quartz plates. 3. Same, after 15 minutes irradiation. 4. After additional 30 minute irradiation. 5. After about 41 hours ageing. 6. After an additional 60 minute irradiation. 7. After additional 105 minute irradiation. The total irradiation time of the film was 210 minutes. Times of exposures: (1), 15 seconds; (2-7), 60 seconds.

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[3] Hess, A. F., and Weinstock, Mildred, *J. Biol. Chem.*, 1925, lxiv, 193.

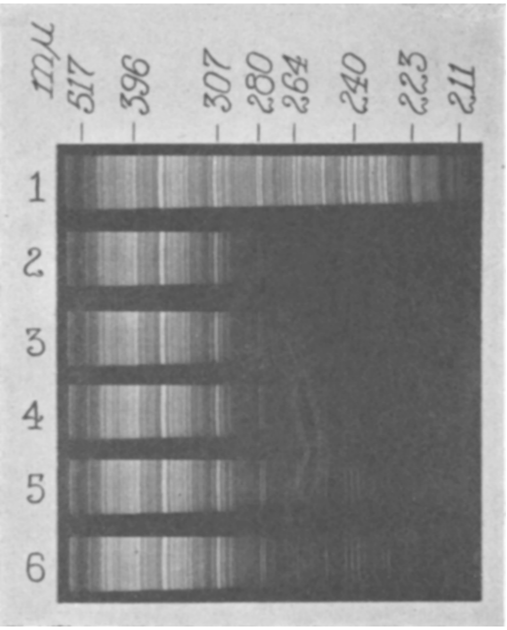

FIG. 6.

1. Spark spectrum. 2. Non-irradiated film. 3. Same, after an interval of 3 hours. 4. After an interval of 18 hours and 30 minutes. 5. Same, after 60 minute irradiation. 6. Same, after additional 60 minute irradiation. Times of exposures: (1), 20 seconds; (2-6), 30 seconds.

a wave length of approximately 256 millimicrons. By increasing the time of irradiation we have found that the transmissibility of crude coal tar is increased to approximately 240 millimicrons for a given concentration. These results naturally raise the question of whether the 2 substances (cholesterol and crude coal tar) do not contain a common ingredient which is responsible for the results obtained. It is possible, although questionable, that cholesterol is present in crude coal tar. At any rate, there is evidence in both cholesterol and crude coal tar of similar chemical changes after irradiation with quartz mercury vapor lamps, as evidenced by changes in transmissibility of ultraviolet radiations. We expect to present further evidence bearing on these points in a later communication.

Conclusions. (1) Ether solutions of crude coal tar show increased transmissibility to ultraviolet light after irradiation by an air-cooled quartz mercury vapor lamp. (2) Ether solutions, on standing, show a decrease in transmissibility. (3) Although an ether solution of crude coal tar is rendered more opaque on standing, it immediately becomes more transparent after irradiation. (4) Thin films of crude coal tar show this increase in transmissibility after irradiation to a more marked degree than does the ether solution of crude coal tar. (5) These changes in transmissibility, detected by changes in the absorption spectra, are regarded as evidences of chemical changes activated by the quartz mercury vapor lamp.

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Some Observations on the Urea Concentration Test.

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Some observations on the phenolsulphonephthalein excretion and urea concentration of the urine in 49 students are here briefly reported. The urea concentration test was carried out entirely as described by MacLean and de Wesselow.[1] The phenolsulphonephthalein tests were carried out in the usual manner, the dye being injected intravenously in all cases and colors matched without the aid of a colorimeter. All the students examined were normal, healthy adults between the ages of 20 and 30. Urinalysis was negative in all cases.

The maximum urea concentration of the urine varied from 2.4% to 4.1%. In 45 of 49 students the concentration varied from 2.5% to 4.0%. The average was 3.22%. Phenolsulphonephthalein excretion varied from 43% to 82.5% with an average of 66.3%.

When the results of the 2 tests in each case are compared a great variation is noted. Curves of phenolsulphonephthalein excretion and the corresponding maximum urea concentration (with the individual determinations arranged in the order of the phenolsulphonephthalein excretion), do not coincide, as they should if they were both quantitative indicators of the excreting power of the kidneys.

In comparing the results of these 2 tests, it must, of course, be remembered that whereas in the dye test the total amount of that dye excreted in 2 hours is measured, in the second test the concentration of urea in a *varying amount* of urine is determined. This fact is recognized in MacLean's instructions that specimens of 120 cc. or over should be discarded as the dilution of the urea is in such

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[1] **MacLean, H., and de Wesselow, O. L. V., *Brit. J. Exp. Path.*, 1920, i, 53.**