A STUDY ON THE CHEMICAL CONSTITUENT OF CHINESE HERB " KIANG HUO"

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"Kiang Huo" (羌活) was originally grown in China. In former times, Dr. Kimura and Nakao [1] ascertained that it belonged to the *Angelica* genus *(Umbelliferae)*. Author was studying at Kyoto University (Japan), we purchased some amount of "Kiang Huo" from a Chinese herb drug market in Osaka for the study of its chemical constituents. [2]

Its morphology is of cyclindrical and annulose shape and dark brown in color. Because of its very brittle nature, it is very easily fractured. Its cross section is rough and black brown in color but with an aromatic smell. Its etherial extract, a dark brown mucilage like substance, cannot crystallize upon cooling. As only limited amount was purchase, it was not possible to make a further research on it.

Recently we collected some "Chuan Kiang Huo" (川羌活) from the Taipei market. Its morphology is very simillar to that of "Kiang Huo". In order to give a systematic study of the umbelliferous drugs, a further research on it was carried out once more.

As the etherial extract did not crystallize upon cooling, it was submitted to silica gel column chromatography. Then by applying the Thin layer chromatography (T. L. C.), we collected the same portion of chloroform and removed the chloroform. But no crystal produced either. However, when treated by saponification as shown in chart I, a crude crystal was obtained. After recrystallization with ethyl alcohol, its melting point raised to 189-190°C The composition of the white needle crystalline (I) is $C_{12}H_{18}O_4$ When the Infra-red spectra of (I) were tested at 1725 cm^{-1}, it showed lactone and carbonyl group.

Based on the foregoing-mentioned melting point, composition and IR spectra, it is presumed that (I) is Bergapten when it was mixed with authentic sample, its melting point did not depress. This fact further strengthened our conviction that (I) is

Bergapten.

Bergapten is isolated from this herb drug by saponification. Ordinarily, *Angelica* genus posses blue fluorescent spots. It shows that this plant contains Umbelliferone. However, merely based on the above-mentioned factors, it still can hardly be determined whether it belongs to the family of *Angelica* genus or not.

Apart from Bergapten, we still continue to study very deliberately other substances.

Experimental Section

Isolation of Bergapten:

Via Taipei drug market, we collected 5kg "Chuan Kiang Huo" (川羌活) which grow in province of Shy Chuan (四川省). It was crushed and mercerated with ether twice for ten days at room temperature. Removing ether and cooling, the etherial extract not crystallized spontaneously. This resin like dark brown extract was submitted to silica gel (Made by Mallinckrodt chemical works) column chromatography. Its eluting solvent of chloroform portion, removing chloroform, there is no crystal produced either. So that carry out Thin layer chromategraphy (T. L. C.), we pick out the same conditional chloroform portion which add 10% KOH in alcohol and set one night for saponification. Then added enough water and removed alcohol by vaccum. Shaking with ether to remove the unsaponification portion.

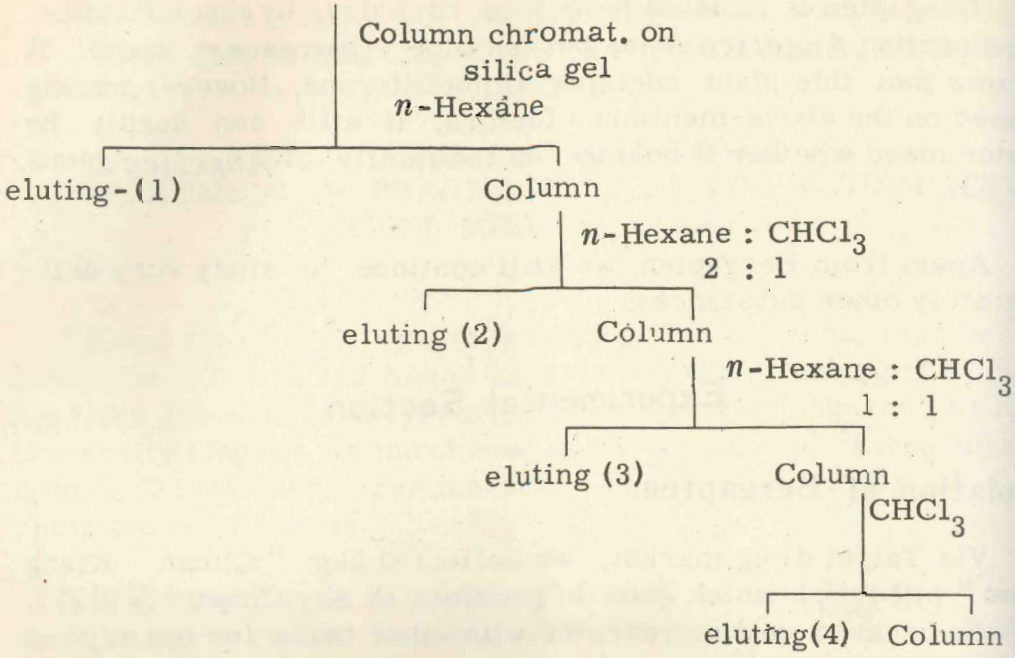
The water layer, acidified by dil. H_2SO_4 and shake out the coumarin fraction by ether. This ether solution is shaked by the following solution: saturated $NaHCO_3$, 5% NaOH. Removing the acidic portion and phenolic portion.

In the neutral portion, dehydration and removing ether, a crude crystall obtained. It treated recrystallization with ethanol, a white needle crystal, mp. 189-190°C (I).

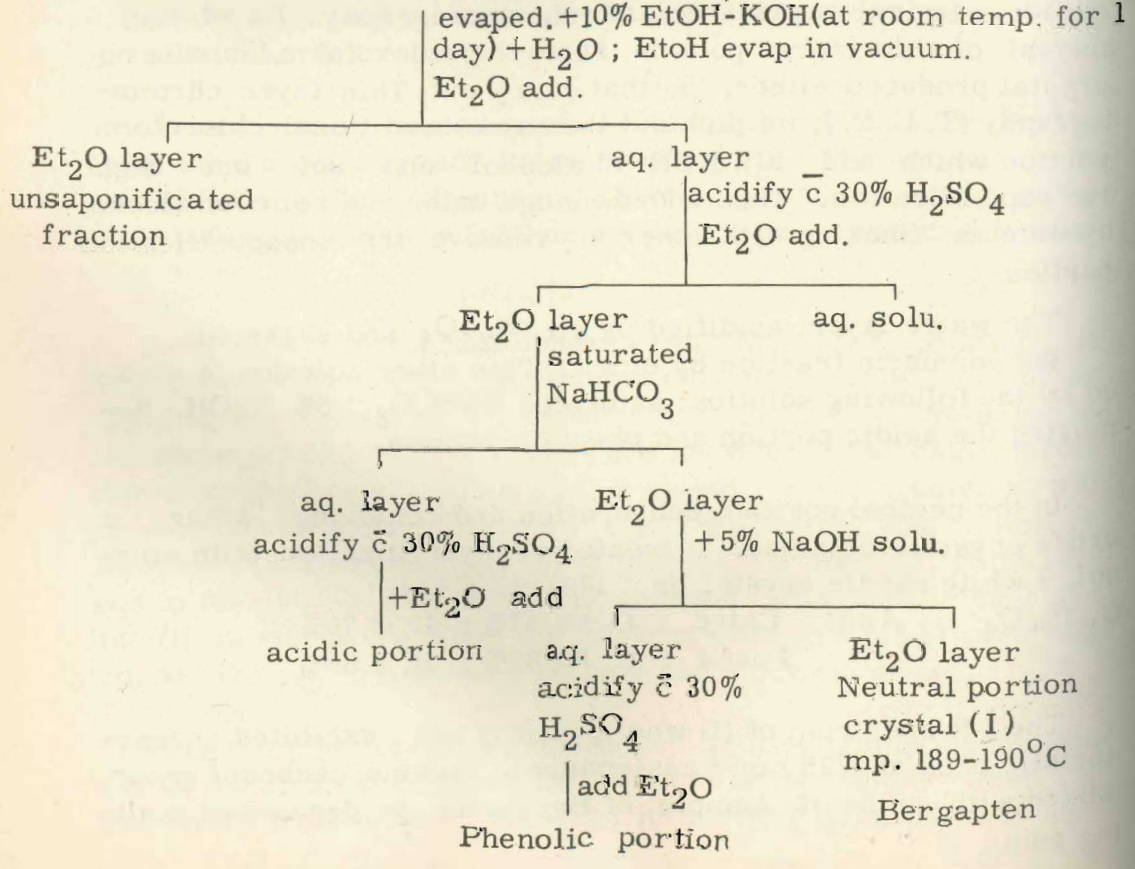
$C_{12}H_{10}O_4$ *Anal.* Calcd : C, 66.67% ; H, 3.70%
Found : C, 66.80% ; H, 3.80%

The I R spectrum of (I) was identical and exhibited characteristic peak at 1725 cm^{-1} assignable to lactone, carbonyl group. Mixed with authentic sample of Bergapten no depressed melting point.

Chart I. Etherial extract of "Chuan Kian-Huo"



Saponification the same chloroform portion



References

1). M. Nakao, K. Kimura: The Annual Proceeding of Shang-hai Natural Science Laboratory Vol. 1, No. 2, 88 (1929).

2). K. Kimura, K. Hata, K. Yen, S. Cheng: Yakugaku Zasshi (Tokyo): 78, 442 (1958).

〔中文摘要〕

羌活之成分研究(I)

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臺北市生藥市場收集之大陸產“川羌活”5公斤，用乙醚(Ether)溫浸抽取，移去乙醚通Silica gel Column Chromatography，展開劑順次用*n*-Hexane，*n*-Hexane：$CHCl_3$（2：1），*n*-Hexane：$CHCl_3$（1：1），$CHCl_3$ oney，將$CHCl_3$部分用T.L.C法將具有有相同Spot之部分合併，皂化後得mp. 189~190°C，組成$C_{12}H_{18}O_4$之白色針狀結晶，由紅外光譜（IR）及與標品混融，融點無下降，證實此結晶爲Bergapten。