

UNCLASSIFIED

AD NUMBER	
ADA801582	
CLASSIFICATION CHANGES	
TO:	UNCLASSIFIED
FROM:	RESTRICTED
LIMITATION CHANGES	
TO: Approved for public release; distribution is unlimited.	
FROM: Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 14 DEC 1945. Other requests shall be referred to Office of Scientific Research and Development, Washington, DC 20301.	
AUTHORITY	
OTS index dtd Jun 1947; OTS index dtd Jun 1947	

THIS PAGE IS UNCLASSIFIED

Reproduced by
AIR DOCUMENTS DIVISION



HEADQUARTERS AIR MATERIEL COMMAND

WRIGHT FIELD, DAYTON, OHIO

The **U.S. GOVERNMENT**

IS ABSOLVED

**FROM ANY LITIGATION WHICH MAY
ENSUE FROM THE CONTRACTORS IN -
FRINGING ON THE FOREIGN PATENT
RIGHTS WHICH MAY BE INVOLVED.**

WRIGHT FIELD, DAYTON, OHIO

REEL - C

1 3 1 7

A.T.I.

3 0 6 3 9

RESTRICTED

Division 9
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

THE PREPARATION OF SOME COMPOUNDS FOR TESTING AS INSECT REPELLENTS

to
October 31, 1945

by
Nathan L. Drake, Charles M. Baker, Glen W. Kilmer
Sidney Melamed, Wilbur J. Shenk and Warren E. Weaver
University of Maryland

Report OSD No. 6370*

Copy No. 55

Date: December 14, 1945

Copy Nos.

- 1 Office of the Executive Secretary
Attention: Chief of Project Control Section
- 2-15 OSD Liaison Office
- 16-23 Navy Department, Office of Research and Inventions
Bureau of Medicine and Surgery
Attention: Lt. Cmdr. J. C. Harper
Lt. Cmdr. J. F. Shronts
Naval Medical Research Institute
Attention: Capt. E. G. Hakansson (MC) USN
Lt. Cmdr. M. Pijoan (MC) USNR
- 24 Naval Research Laboratory
- 25 Brigadier General Eugene A. Regnier, War Department
Liaison Officer for the NDRC
- 26 Office of the Chief of Chemical Warfare Service
Attention: Chief, Technical Division
- 27-30 Commanding General, Chemical Warfare Service
Technical Command, Edgewood Arsenal, Maryland
- 31-32 Office of the Quartermaster General
Army Service Forces, Washington 25, D. C.
Attention: Brigadier General Georges F. Doriot
(Mr. William H. Lee)
- 33-34 Office of the Chief of Engineers
Army Service Forces, Washington 25, D. C.
Attention: Captain H. D. Reed
- 35-37 Office of the Surgeon General
Army Service Forces, Washington 25, D. C.
Attention: Lt. Col. John B. Klopp
(Col. Emory C. Cushing)
(Lt. Col. Oliver R. McCoy)

RESTRICTED

RESTRICTED

Copy Nos.

38-41	National Research Council, Insect Control Committee
42	Dr. F. C. Bishopp, Bureau of Entomology and Plant Quarantine, USDA
43	Mr. H. H. Stago, Bureau of Entomology and Plant Quarantine, USDA
44	Dr. H. L. Haller, Bureau of Entomology and Plant Quarantine, USDA
45	Mr. E. F. Knipling, Bureau of Entomology and Plant Quarantine, USDA
46	Dr. Walter R. Kirner, Chief, Division 9, NDRC (Division 9 Files)
47	Dr. Homer Adkins, Member, Division 9, NDRC
48	Dr. Arthur C. Copo, Member, Division 9, NDRC

Total Number of Copies - 55

* National Research Council Insect Control Committee Report No. 153

This document contains information affecting the national defense of the United States within the meaning of the Espionage Act, U.S.C. 50; 51 and 32. Its transmission or revelation of its contents in any manner to an unauthorized person is prohibited by law.

RESTRICTED

RESTRICTED

OSRD No. 6370

DIVISION 9
NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

THE PREPARATION OF SOME COMPOUNDS FOR TESTING AS INSECT REPELLENTS

Service Directives CWS-32 and SO-6

Endorsement (1) Dr. Joseph Dec, Technical Aide, Division 9 to Dr. Walter R. Kirner, Chief, Division 9.

Forwarding report and noting:

"Reported herein is the submittal of 651 organic compounds, mixtures and creams for testing as insect repellents. The report includes directions for preparation of these materials, their insect repellency testing data and a discussion of the relationship of chemical structure and physical properties to insect repellent effectiveness.

"Among the promising candidate insect repellents tested after application to skin O-6133, O-6154, O-6168, O-6216, O-6230 and O-6252 have "passed" acute toxicity tests and have been submitted for 90-day subacute toxicity studies. O-6109, O-6152, O-6217, O-6226, O-6254 and O-6263 have "passed" (some with reservations) acute toxicity tests but have not been submitted for 90-day subacute toxicity studies. O-6210, O-6316, O-6319, O-6358, O-6397, O-6484, O-6498, O-6500 and O-6503 have been submitted for acute toxicity tests, still to be completed. Seventy-one other compounds whose average repellency times ranged from 181 to 352 minutes against *Aedes aegypti* were not submitted for acute toxicity tests. Among the compounds tested after impregnation in cloth fourteen were repellent against *A. aegypti* more than ten days.

"When the NDRC, Division 9 program on the preparation of candidate insect repellents was terminated shortly after the end of the war with Japan insect repellency data from the field and further toxicity data were needed to evaluate adequately the promising candidate insect repellents prepared under this contract. Toxicity studies are being made. Additional quantities of some of the promising compounds would have to be prepared for repellency tests in the field and toxicity studies.

"The insect repellency data were obtained by the U. S. Department of Agriculture, Bureau of Entomology and Plant Quarantine,

RESTRICTED

RESTRICTED

Division of Insects Affecting Man and Animals at Orlando, Florida. The irritancy and toxicity data were obtained by the Food and Drug Administration, Division of Pharmacology in Washington, D. C. and are presented in detail in their reports.

"The studies described in this report were part of a NDRC, Division 9 program (OSRD Formal Reports No. 5285, 6367, 6368, 6369, 6370, and 6371) to find insect repellents more effective than the G-2-2 mixture used by the Armed Services. The insect repellency data in the aforementioned reports and other insect repellency data are given in reports by the Bureau of Entomology and Plant Quarantine and the Naval Medical Research Institute."

(2) from Dr. Walter R. Kirner, Chief, Division 9 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report with approval.

This is a final report under Contract 9-494 OELsr-1503 with the University of Maryland.

RESTRICTED

RESTRICTED

TABLE OF CONTENTS

	Page
I. Summary	
II. Introduction	1
III. Status of Studies	2
IV. Relationship of Chemical Structure and Physical Properties to Insect Repellency	5
V. Insect Repellency Testing Data	29
VI. Experimental	77
VII. Appendix - Analysis of Candidate Esters Prepared by Shank	87

RESTRICTED

RESTRICTED

SUMMARY

1. As of October, 1945, 631 compounds, mixtures and creams were submitted as candidate repellents. More than 600 of these were individual compounds. Of this number 109 were repellents; these compounds passed the minimum requirements (180 minutes to the first bite vs. Aedes or 120 minutes vs. Anopheles or 10 days to the first bite vs. Aedes in cloth tests).

2. Our results have led to the conclusion that in selecting a candidate repellent consideration should be given to boiling point and functionality. In general a candidate should have a boiling point in the range of 90-130°C/0.5 mm. and should be polyfunctional. In one group, chosen with regard to these criteria, 54% of the candidates submitted were repellent.

3. It would appear that the limiting factor to repellent time is the rate of absorption of the repellent by the skin rather than the volatility or chemical structure of the repellent. Absorption thus seems to set an upper limit of about 400 minutes on repellent time.

RESTRICTED

INTRODUCTION

The work on this project, directed toward the development of a satisfactory mosquito repellent, was begun in June, 1944. The ideal repellent as defined by the Army was to be odorless, or have a mild odor, have no undesirable characteristics on application to the skin, be non-toxic and be repellent to all species of mosquitoes for at least twelve hours. At the time that our work began a large number of individual chemicals and industrial products had been tested for insect repellency at Orlando, Florida. These results were compiled and arranged according to chemical groups and served as a basis for future work. The Army had in current use a repellent, 622, which was effective for about two hours.

The first procedure adopted in the selection of candidate repellents, for lack of a theory relating structure to repellency, was the preparation of homologs and analogs of compounds which had indicated repellent properties. The second procedure was the selection and preparation of compounds for which there were no precedents, this procedure being a random search for suggestions for future work. The results of all cooperating laboratories were made currently available through the medium of a card index distributed by a coordination center. On the basis of accumulated data certain chemical and physical prerequisites of a repellent were developed and were used in the later selection of candidates. A list of proposed candidates was submitted before preparation to the coordination center to avoid duplication in preparation.

Compounds selected as candidates were prepared in amounts of 30 g. each for preliminary tests for irritancy and repellency. Five gram samples were submitted, after October, 1944, to the Pure Food and Drug Administration in Washington for preliminary irritancy tests. Simultaneously 25 g. samples were sent to Dr. Knipling at Orlando, Florida for repellency tests. Compounds which were of interest were requested in amounts of 500 g. for acute toxicity tests and further repellency tests. Those compounds which were relatively non-toxic and still were of interest because of their repellency values were then requested in amounts of 4 l. Three liters was submitted for chronic toxicity tests and one liter for further repellency testing at Florida and overseas.

Since our primary objective was the preparation of large numbers of compounds in an effort to survey rapidly the types of chemical compounds, no attempt was made to characterize completely the compounds prepared or to investigate reactions or products which would have been of interest in a classical approach. The compounds submitted were prepared in a state of purity usually better than 95% and characterized sufficiently to establish their identity. In cases where the product was of continued interest and its identity or purity was in doubt, further work was carried out to fully establish its identity and purity.

Inasmuch as our laboratory was equipped for chemical synthesis, we often cooperated with other investigators by preparing quantities of chemicals for their needs.

An attempt has been made to use the latest Chemical Abstract names in the naming of compounds throughout this report.

STATUS OF STUDIES

It is the purpose of this section to outline the state of our work at the time of contract termination and to indicate where further work may be desirable. A list has been prepared of all compounds submitted for acute toxicity studies and their status indicated by P = passed, C = caution or NP = not passed. At the time the report was in progress data were not available for all these compounds. A similar list has been prepared of the six compounds prepared in amounts of 4 l. and submitted for chronic toxicity studies; no data have been received for these compounds. All those compounds which seemed to warrant further consideration on the basis of acute toxicity and repellency data have been submitted for chronic toxicity studies. Of those compounds submitted for acute toxicity on which no data are as yet available, the following three compounds would be of particular interest if the toxicity testing data are favorable:

- 6316 1,6-Hexanediol, diacetate (if further tests against Anopheles substantiate the DMP ratio of 2.6)
- 6498 Cyclohexanecarboxylic acid, 1-hydroxy-, 2-butoxyethyl ester
- 6503 Ethanol, 1-phenyl-2-propoxy-

Of the many compounds which were repellent but were not submitted for further testing, the following two are deemed of special interest to be prepared for acute toxicity studies:

- 6526 1,2-Ethanediol, 1-phenyl-, 2-propionate
- 6135 Caprylic anhydride

In connection with this review of the current status of our work, it may be of interest to list the laboratories with which we have co-operated so that a complete file of the data relating to our compounds can eventually be prepared.

Table I

Groups Receiving Samples Directly

Dr. Copley, Norwich Pharmacal Co., Norwich, N. Y.
Dr. Haller, Bur. of Entomology and Plant Quarantine, Beltsville, Md.
Dr. Knipling, Bur. of Entomology and Plant Quarantine, Orlando, Florida
Dr. Parker, Rocky Mountain Laboratory, Hamilton, Montana
Lt. Pi Joan, Naval Medical Research Institute, Bethesda, Md.
Dr. Smith, Food and Drug Administration, Washington, D. C.
Dr. Spruyt, National Academy Research Council, Washington, D. C.
Dr. Yeager, Committee on Inter American Affairs, Washington, D. C.

Further work on new candidate repellents is indicated from our results, however the scope of such work is too great to be discussed in the present report, and could more profitably be done by the group contemplating a continuation of the program.

Table II

Compounds Submitted for Acute Toxicity Studies

Orlando Number	Name	Status
6152	Butyric acid, 3-phenylpropyl ester	P
6263	1,5-Pentanediol, diacetate	C
6154	1,5-Pentanediol, dipropionate	C
6316	1,6-Hexanediol, diacetate	
6319	1,6-Hexanediol, dipropionate	
6109	Furoic acid, furfuryl ester	C
6230	Acetoacetic acid, cyclohexyl ester	F
6254	1,3-Cyclohexanediol, monopropionate	C
6500	Cyclopentanecarboxylic acid, 1-hydroxy-, 2-butoxyethyl ester	
6133	Cyclohexanecarboxylic acid, 1-hydroxy-, cyclopentyl ester	P
6493	Cyclohexanecarboxylic acid, 1-hydroxy-, 2-butoxyethyl ester	
6226	Cyclohexanecarboxylic acid, 1-hydroxy-, butyl ester	P
6220	Hydraacrylic acid, β -phenyl-, methyl ester	NF
6216	Hydraacrylic acid, β -phenyl-, ethyl ester	F
6217	Hydraacrylic acid, β -phenyl-, isopropyl ester	C
6503	Ethanol, 1-phenyl-2-propoxy-	
6210	6-Dodecanone, 7-hydroxy	
6168	Succinamic acid, N,N-diethyl-, propyl ester	P
6252	Succinamic acid, N,N-dipropyl-, ethyl ester	P
6353	Glutaramic acid, N,N-diisopropyl-, ethyl ester	
6397	Glutaramic acid, N,N-diisopropyl-, propyl ester	
6484	Adipamic acid, N,N-diisopropyl-, methyl ester	

Table III

Compounds Submitted for Chronic Toxicity Studies

Orlando Number	Name
6154	1,5-Pentanediol, dipropionate
6230	Acetoacetic acid, cyclohexyl ester
6133	Cyclohexanecarboxylic acid, 1-hydroxy, cyclopentyl ester
6216	Hydraorylic acid, β -phenyl-, ethyl ester
6168	Succinamic acid, N,N-diethyl-, propyl ester
6252	Succinamic acid, N,N-dipropyl-, ethyl ester

RELATIONSHIP OF CHEMICAL STRUCTURE AND PHYSICAL PROPERTIES

TO INSECT REPELLENCY

Everyone who has participated in the work directed toward the development of a repellent has immediately noticed some apparent correlation between a physical or chemical property and repellency. In general, however, these early relationships did not seem to be adequate; numerous exceptions were rapidly evident, until finally the proposed relationship was abandoned. It has been our experience that the only fertile approach was a statistical one and that certain relationships when applied to the selection of candidate repellents would consistently result in obtaining a higher percentage of repellents, but at no time were the results absolute.

Since our approach will be statistical in discussing the factors which we believe are helpful in choosing a candidate, it will be necessary to consider the source and validity of the repellent data and physical constants upon which we base our conclusions.

The people who have worked with mosquitoes have continually emphasized the variability of the data and the many factors which must be considered in standardizing test conditions. Our own observations concerning the factors affecting repellency data are culled from the many reports that we have received and from the large amount of data on compounds submitted for repellency tests. We would like to record these observations under three groups, factors affecting the mosquito, factors affecting the amount of repellent on the arm, and finally variations in data as we have received it.

In noting the factors affecting the mosquito, we wish merely to list those factors that we have been made aware of by reading various reports. The frequency of testing, the acquired tolerance of the mosquito for the repellent, the age, species and sex of the mosquito, the conditions of light or darkness, temperature and humidity, the apparent seasonal variation, all these and no doubt other factors, influence the results of tests. For example, DeLong (Monthly Report No. 9) reports the amazing result that at 37° and 100% relative humidity mosquitoes are not attracted by the human and that attraction depends upon a temperature and humidity differential between the skin and the atmosphere. Again, in support of seasonal variation, we have noticed that during certain months the data received from Orlando have been uniformly low for all cooperating laboratories, while at other times the percentage of repellent compounds is greatly increased.

Of the factors affecting the amount and distribution of the repellent on the arm, the individual variation of the test subject is immediately apparent. The care of application, required to insure an even distribution of repellent, the size of the forearm, the amount of hair present are important variables. The rate of absorption (which varies with the individual, the temperature, which influences the rate of peripheral circulation, and the type of the compound being tested) is perhaps the

most important factor in the breakdown of repellent materials. A study has been made by the British (Sir R. Christophers - British Report) of the relation of surface tension and of viscosity to repellency. Repellency did not seem to vary in any regular fashion with surface tension, but viscosity was directly related. There appeared to be an optimum viscosity which would hold "creep" to a minimum and yet not prevent ready and thorough spreading upon application. "Creep" was responsible for a draining of the repellent with the formation of bare areas and attendant early breakdown. Volatility of the repellent did not appear to be an important factor influencing the amount of repellent except as the odor affected mosquitoes. The testing of candidates under sweating conditions and mechanical removal by contact, clothes or rain also affect the amount and distribution of repellent.

The data as received from Orlando were of three types, results on liquids tested directly on the forearm and expressed in minutes, results on solids and irritant liquids tested on cotton hose worn on the arm (these results expressed in days), and so-called paired tests in which the compound is tested simultaneously with a sample of dimethyl phthalate and the results expressed in minutes reported for both. These last results are often expressed as a "dimethyl phthalate ratio" where the value of dimethyl phthalate forms the denominator. By convention liquid compounds with repellent times of more than 179 minutes against *Aedes* or 119 minutes against *Anopheles* are considered repellent while solids or irritant liquids tested on cloth with repellent times of 10 days or more are termed repellent. In general paired tests are conducted only with repellent materials. The value of 10 days adopted for solids is roughly equivalent to the values used for liquids.

A third group of observations which indicate the reliability of the data is the variation in the data as reported. Numerous examples may be cited to show the general consistency of results and the validity of using the data in an analysis. However to indicate the range of variation and to form a foundation to explain some apparently anomalous results, examples will be cited of apparent inconsistencies in data. The first and perhaps a trivial example is the occurrence of errors in arithmetic and transcription. Obvious errors are those where the mean values recorded are outside of the limits of either extreme. It may be well to note at this point that the data as received records the number of trials, the range in values, and the average value. Errors in transcription are sometimes made evident by duplicate reports of data. An example of day to day variability, which could lead to anomalies in analysis is the following:

Orlando

Number	Original Results	Resubmitted sample	Paired Tests
6375	<i>Aedes</i> 2(95-135) <u>115</u> <i>Anoph.</i> 2(16-31) <u>24</u>	4, <u>260</u> 4, <u>40</u>	4, <u>305/275</u> 4, <u>43/61</u>

The underlined numbers are the average values; the denominator in the case of the paired tests is dimethyl phthalate. An example of variability on cloth, where one might expect some of the variables to be eliminated, is

phenxyacetic acid which in one series of tests averaged more than 20 days and in a second series averaged zero days. An illustration of another type of variability is the following example of a compound, repellent on the arm, but ineffective on cloth - a rather surprising result,

Orlando Number	Skin Value	Cloth Value
6251	8. 218	0 days (5th bite)

It was hoped that the introduction of paired tests would lead to entirely reproducible ratios. Perhaps the choice of dimethyl phthalate as a comparison substance was unfortunate, but the results are no more consistent than others. Here it will be observed that the ratio

Orlando Number	Original Results	Subsequent Tests
5563	Aedes 443/275 = 1.61 Anoph. 198/53 = 3.74	517/389 = 1.33 193/140 = 1.36

when Anopheles are used varies by a factor of 2.7. In cases where a series of compounds are submitted, the recalcitrant member may be readily detected and resubmitted, but where only a few or one member of a group is submitted, its true value may be overlooked.

We have thus considered in three groups some of the factors which influence the validity of repellent data. Of these factors we believe that the phenomenon of absorption of the repellent by the skin is the single factor most responsible for limiting repellent time. The question of volatility arises and its role as a limiting factor. Comparative studies have been made by Sulzberger (NRC - I.C.C.R. No. 113) on the amount of dimethyl phthalate recoverable from the skin and from a piece of cloth exposed to the same conditions of temperature and humidity. The cloth showed only slight loss in a matter of days while the repellent was present to the extent of only 36% after five hours on the skin. Comparable quantities were applied to skin and cloth. A further example in point is the observation that further applications of repellent, at intervals preceding breakdown of repellency, will extend the repellent time considerably. These and similar results have lead one investigator (Elishewitz-private communication) to state that all "repellents" were equally good, the question was how to keep them on the skin. This led to the development of creams and films designed to retain the repellent. For example Sulzberger showed that an ointment compounded with dimethyl phthalate retained 90% of its content of repellent in a five hour period under similar conditions to those described above. Although these creams and films materially increased repellent time they were unpleasant to use and therefore not practicable.

The above discussion might logically lead to the question of what kind of compound should be used as a repellent. The first results indicated that not all materials were repellent, in fact on a random basis only 8-10%

of all materials submitted were repellent. From the above remarks one might conclude that a high boiling, poorly absorbed compound of medium viscosity and low water solubility would be the answer. Our results and those of others however establish the fact that only compounds boiling in a rather narrow range can usually be repellent. This is a necessary but not sufficient condition and leads to the question of what structure plays in determining repellency.

At this point it may be well to discuss the validity of the physical data reported which forms the basis for the conclusion that boiling point is an important parameter in determining repellency. In general the values designated in our report as boiling points were those recorded during the distillation, attendant on purification, of materials submitted as repellents. These distillations were carried out in many different types of columns under varied conditions, and the results therefore are not strictly comparable. Generally, however, we believe that the values would be correct to within 10° or less which is of sufficient accuracy for our purposes. The ideal set of values would have been the vapor pressures as determined at 37° , but this determination was not practicable. We have chosen boiling points at 0.5 mm. wherever possible and corrected others, for purposes of comparison, to that value using the approximate relationship that boiling point decreases 10° for each halving of the pressure.

An analysis of all esters submitted up to February, 1945 was made (Appendix). Of all such compounds submitted, 9% were repellent. By limiting the compounds to those having molecular weights of 175-249 the number of repellents rose to 16%, an increase of 75%. Ninety-two percent of all repellent esters fell in this molecular weight range, which is roughly equivalent to a boiling point range of similar extent. Early in the program a statistical analysis of the compounds then tested was prepared by Wadley (Summary Report, 11-20-44) who concluded with the observation, "it is possible that eventually we can define a certain range in the middle of a series, and find that within it we have successful and unsuccessful repellents; outside of the range, only unsuccessful ones." Similarly, a list of compounds submitted as candidate repellents by Orlando (Jones, private communication) was prefaced by the statement, "and boiling points between 200 and 300° . Several of our good repellents have ---- boiling points in this range." This necessary condition was thus early recognized by other workers. Experience with data of homologous and analogous series has indicated that the inclusive range for boiling point is $80-130^{\circ}/0.5$ mm. This, no doubt, could be narrowed for individual series and by more accurate data. To illustrate this conclusion we have included in Table IV a listing of all repellent hydroxy-esters and amide-esters submitted from this laboratory with their boiling points, corrected in some cases, at 0.5 mm. Considering the extensive range of boiling point possible, the specificity is quite striking. Very few repellent compounds lie outside of this range, however the converse is not true. "Any compounds which possess boiling points in this range are non-repellent, and this fact gives rise to a consideration of structure. One further point that is of interest is the fact that each type of compound when submitted as a homologous series shows a repellent peak or plateau.

Table IV

Hydroxy Esters

6103	88 ⁿ
6333	85
6378	125
6317	95
6387	131
6254	93
6257	110
6602	91
6526	111
6145	96
6499	89
6551	107
6139	85
6138	97
6500	98
6136	39
6133	74
6134	107
6608	113
6494	94
6498	113
6596	125
6201	87°/2.0
6225	93
6226	101
6599	100
6500	108
6220	112
6216	112
6218	119
6217	115
6221	112
6224	105

Amide Esters

6166	100°
6168	100
6172	99
6388	106
6246	125
6328	118
6252	101
6251	117
6393	120
6348	105
6350	98
6390	109
6395	105
6336	127
6369	102
6373	114
6365	116
6375	104
6358	109
6397	117
6511	105
6484	110
6310	107
6312	100
6603	81
6605	101
6461	90
6514	33
6601	106
6563	101
6604	114
6465	88

These maxima always fall in the boiling point range described above, but, in terms of repellent time, all maxima are approximately equal. One might interpret this result, and justifiably, as indicating that there is an effective upper limit to repellent time, and while many repellents are still to be found none will exceed previous repellents in activity. However, from other fields of application, one is constantly reminded of the unique which disproves the rule, and hence, the statement is merely appended as an observation summarizing current results.

The relationship of chemical structure to repellency is the remaining question. Here the answer is diffuse and complicated by the fact that every group has at least one representative repellent. No single structure or group of structures or any relationship between groups has been shown to be responsible or essential for repellent action. The most successful approach has been to answer the question - what group or groups are most likely to produce repellent activity.

A side issue would be an effective correlation of absorption and chemical structure, but the data available are not conclusive or even suggestive. An interesting experiment which gives some indication of the relative rates of absorption is the recording of repellent time to the fifth and seventh bites. Noticeable differences were observed which could be attributed only to absorption since evaporation was not significant during such a relatively short time interval. Perhaps this method could be extended to obtain data correlating absorption with chemical structure.

A cursory examination of the data arranged according to chemical groups readily makes apparent certain groups which seem more promising. It is obvious from such an examination that hydrocarbons as a group are non-repellent, as are simple monofunctional esters. Similarly it would appear that acids, amides, and glycols among others are promising fields for further effort. An early suggestion was that compounds be prepared which in themselves were non-repellent but would by oxidation or hydrolysis liberate slowly an active compound. Such suggestions led to the preparation and testing of aldehydes, since acids were effective; and acetals of 1,2 and 1,3-glycols, since many such glycols were active. In most cases where activity was observed, the active material was the original substance and had a boiling point in the proper range.

A complete answer to the question at hand would be obtained only by a systemic statistical survey of all compounds submitted and a revision of such a survey at frequent intervals. This was done in the case of esters by Shenk (Appendix), and a summary of his results indicates the value of the method. Having found that 90% of all repellent esters had a molecular weight between 175-249 a comparison was made of repellent and non-repellent esters in this molecular weight range. These esters were compared according to the number of functional groups present, including any cyclic structure as a functional group. It is observed that 87% of all repellent esters possess three or more functional groups, while only 54% of all the esters are trifunctional. Another comparison showed that of the trifunctional esters 26% were repellent. Thus by imposing functionality and molecular weight as parameters for repellency the chances of

obtaining a repellent was increased from 9% to 26%, an increase of 188%. Only 4.7% of the difunctional compounds tried were repellent.

A further comparison of trifunctional esters reveals the striking effect of the hydroxyl group which increases the possibilities of obtaining a repellent to 56%; the procedure extended to hydroxy-esters shows that the cyclo-group is also effective. These last two conclusions are based on a relatively small amount of data and hence the reliability of the percentages is somewhat lower than those first reached. On the basis of these results a number of cyclo-hydroxy-esters of proper boiling point have been submitted, and it is interesting to note that about 52% of these were repellent. Although this figure could obviously still be improved, the figure does represent a considerable increase over the 9% originally obtained for esters as a group.

We believe that this approach will be equally effective when applied to other groups. At this point we come to the conclusion that all the factors are not evident. One explanation to which we may have recourse is to concede powers of discrimination to the mosquito, but of course this does not answer the question.

To conclude therefore that a compound to be repellent must have a boiling point within a specified range and preferably should be polyfunctional. We have also shown that within these limits the process of absorption appears to provide a limit to repellent activity.

During the course of our work we have empirically found several groups of compounds which yielded relatively large numbers of repellents. In addition to the hydroxy-esters, glycol diesters and amide esters were investigated rather extensively. Several of the glycol diesters showed repellency against *Anopheles* and hence were of interest. As a group however they did not yield a high percentage of successful candidates. On the other hand the preparation of amide-esters resulted in a high percentage of repellent candidates. Of the 76 amide-esters prepared, not including urethanes which are a special case, 42% were repellent. This number does not consider the added limitation of boiling point, a factor which would definitely increase the percentage of repellents. Forty-three percent of all hydroxy esters tested were repellent whereas 52% of all cyclo-hydroxy-esters were successful. Thus the validity of our earlier conclusions becomes apparent.

To further emphasize these results the figures obtained when these rules are ignored are of interest. Of 64 simple esters submitted, which violate the condition of polyfunctionality, only one was repellent, an average of 0.2%. Of the remaining groups that were tried keto-esters were in general not effective, while amine-esters, especially of the glycine type, indicated some promise.

A tabulation of all repellent compounds submitted has been included in Table V. It will be recalled that repellents are all compounds whose average value against *Aedes* is greater than 179 or whose average value against *Anopheles* is greater than 119 or whose value on cloth is better

RESTRICTED

12.

than 10 days. Some compounds are included whose later tests indicate that they are not repellents. They are included in order to report "paired-test" data which are available. It will be noticed that the activity shown against Anopheles, and the total amounts submitted are included. The toxicity data refer to acute toxicity tests and are the same as those shown in an earlier table. Paired test data are included as a ratio and the value of the ratio is also given. In some cases paired test data available from different samples are included separately. In the case of cloth tests the value is given in days; small d indicates days. The structures are included to facilitate visual comparison of the data. The values given under repellent time show the number of tests, and the average repellency. The range is included in Table VII.

RESTRICTED

Table V

Repellent Compounds

Orlando Number	Name and Structure	Repellent Time		Acute Toxicity	Amount Submitted
		Aedes	Anopheles		
6142	β -Isoduraldehyde <chem>CH3CH2CH(C2H5)COOH</chem>	12 (176)	12 (108)		70 g.
6171	Eutyric acid, α -ethyl- <chem>CH3(CH2)4CH2COOH</chem>	13 (122)	12 (67)		20 g.
6170	Enanthic acid <chem>CH3(CH2)8CH2COOH</chem>	14 (165)	18 (104)		50 g.
6117	Heptadecanoic acid <chem>CH3(CH2)14COOH</chem>	17 (318)	17 (115)		30 g.
6290	Lauric acid <chem>CH3(CH2)10COOH</chem>	16 d	0 d		20 g.
6302	Cyclohexanecarboxylic acid, 1-hydroxy	20 + d	2 d		20 g.
6235	Benzic acid <chem>C6H5COOH</chem>	12 d	0 d		20 g.

RESTRICTED

RESTRICTED

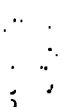
13.

Orlando Number	Name and Structure	Repellent Time		Acute Toxicity	Amount Submitted
		Aedes	Anopheles		
6295	$C_6H_5OCH_2COOH$	20 + d	0 d		
6296	Acetic acid, phenoxy- 	0 d (2nd sample)	0 d		275 g.
		10 d	0 d		
6135	Salicylic acid	3 d (2nd sample)	0 d		70 g.
		12 (271)	12 (81)		
6152	Caprylic anhydride	4 (359/279=1.29)	4 (97/181=0.54)		175 g.
		18 (386)	17 (61)		
6115	Butyric acid, 3-phenylpropyl ester	4 (169/298=0.57)	6 (41/41=1.00)	P	560 g.
		11 (131)	15 (92)		
6263	1,3-Propanediol, diisobutyrate	4 (179/277=0.64)	3 (105/261=0.40)		50 g.
		22 (167)	22 (81)		
6154	1,5-Pentanediol, diacetate	4 (207/296=.68)	4 (101/106=.95)		550 g.
		27 (170)	31 (98)		
6383	1,5-Pentanediol, dipropionate	5 (281/226=1.24)	7 (140/146=0.9)	C	5 l.
		8 (259)	8 (65)		
6316	1,5-Fentanediol, dipivalate	4 (221/288=.78)	4 (58/99=.62)		35 g.
		8 (243)	8 (135)		14.
	1,6-Hexanediol, diacetate	4 (253/318=.80)	4 (142/60=2.6)		550 g.

RESTRICTED

RESTRICTED

RESTRICTED

Orlando Number	Name and Structure	Repellent Time Aedes	Anopholes	Acute Toxicity	Amount Submitted
6319	$(CH_3CH_2CO_2 \cdot CH_2CH_2CH_3)_2$ 1,6-Hexanediol, dipropionate	12 (158)	12 (107)		550 g.
6337	$(CH_3CO_2CH_2CH_2CH_2CH_2CH_3)_2$ 1,9-Nonanediol, diacetate	10 (224)	10 (75)		30 g.
6236	 1,3-Cyclohexanediol, diacetate	8 (216)	6 (72)		30 g.
6355	 Malonic acid, butylethyl-, diethyl ester	8 (141)	8 (41)		30 g.
6665	$(CH_3CH_2CO_2CH_2CH=CH_2)_2$ Adipic acid, diallyl ester	14 (95)	14 (54)	NP	300 g.
6496	$CO_2CH_2C_4H_7O$ $COO \cdot C_6H_5$ Cyclopentanecarboxylic acid, 1-acetoxy-, tetrahydrofurfuryl ester	10 (304)	10 (47)		30 g.
6507	$CH_3OC_6H_4CO_2CH_3$ Anisic acid, methyl ester	20 + d	4 d		30 g.
6099	$CH_3CC_6H_4CC_6H_4 \cdot CH(CH_3)_2$ Anisic acid, isopropyl ester	5 (198)	5 (69)		80 g.

15.

RESTRICTED

RESTRICTED

16.

Orlando Number	Name and Structure	Repellent Time		Acute Toxicity	Amount Submitted
		Aedes	Anopheles		
6109	$C_4H_3O \cdot CO_2CH_2 \cdot C_4H_3O$	9 (177)	10 (42)		
6113	Furoic acid, furfuryl ester $CH_2CH_2CC_2 \cdot CH_2 \cdot C_6H_4OCH_3$	2 (126/194=0.65)	2 (42/47=0.89)	C	550 g.
6169	Propionic acid, p-methoxybenzyl ester $C_3H_7 \cdot CO_2CH_2 \cdot C_6H_3O$	5 (215/276=0.78)	5 (69/141=0.49)		50 g.
6022	Caproic acid, tetrahydrofurfuryl ester $C_6H_5CO_2CH_2 \cdot C_4H_7O$	9 (212)	11 (127)		30 g.
6440	Benzoin acid, tetrahydrofurfuryl ester $CH_3 - O - C(CH_3)_2 - CH_2CO_2C_6H_{11}$	4 (244/233=1.05)	4 (184/196=0.94)		30 g.
6502	1,3-Dioxolane-2-acetic acid, 2-methyl-, cyclohexyl ester $CH_3OCH_2 - CH_2 - O - C(CH_3)_2 - CH_2CH_2CO_2C_6H_5$	21 (273)	22 (65)		30 g.
6238	1,3-Dioxolane-2-propionic acid, 4-(methoxymethyl)-2-methyl-, ethyl ester $O = C - O - C(CH_3)_2 - CH_2CH_2CO_2C_2H_5$	8 (181)	8 (33)		30 g.
	1,3-Dioxolane-2-one, 2,2-dimethyl-5-phenyl- $O = C - O - C(CH_3)_2 - CH_2CH_2CO_2C_6H_5$	10 (247)	10 (45)		30 g.
	1,3-Dioxolane-2-one, 2,2-dimethyl-5-phenyl- $O = C - O - C(CH_3)_2 - CH_2CH_2CO_2C_6H_5$	4 (278/249=1.12)	4 (44/59=0.75)		350 g.

RESTRICTED

RESTRICTED

17

Orlando Number	Name and Structure	Repellent Time		Acute Toxicity	Amount Submitted
		Aedes	Anopheles		
623C	$\text{CH}_3\text{COCH}_2\text{CO}_2\text{C}_6\text{H}_{11}$	41 (101)	39 (57)		
	Acetoacetic acid, cyclohexyl ester	4 (177/302=0.59) 2 (107/125=0.86)	4 (128/144=0.89) 2 (45/65=0.69)		5 l.
6472		17 (250)	17 (56)		
6535	Cyclopentane-1-carboxylic acid, 2-oxo-cyclopentyl ester.	8 (274/245=1.12)	8 (49/62=0.79)		30 g.
		14 (181)	4 (55)		
6534	2-Cyclohexene-1-carboxylic acid, 2,6-dimethyl-4-oxo-, ethyl ester	4 (286/251=1.14)	4 (59/65=0.91)		50 g.
		12 (203)	12 (41)		
6103	2-Cyclohexene-1-carboxylic acid, 6-ethyl-2-methyl-4-oxo-, ethyl ester	4 (258/199=1.30)	4 (37/44=0.84)		30 g.
	$\text{C}_5\text{H}_{11}\text{CO}_2\text{CH}_2\text{CH}_2\text{OH}$	11 (200)	11 (60)		
6333	Glycol, monoacrylate	1 (177/180=0.98)	1 (44/55=0.80)		50 g.
	$\text{C}_5\text{H}_{11}\text{CO}_2\text{CH}_2\text{CHOCH}_3$	8 (209)	8 (80)		
6094	1,2-Propanediol monoacrylate	4 (229/174=1.33)	4 (78/128=0.61)		30 g.
	$\text{C}_5\text{H}_{11}\text{CO}_2\text{C}_3\text{H}_7\text{OH}$	6 (207)	6 (37)		
	1,3-Propanediol monoacrylate	2 (289/214=1.35)	2 (59/45=0.87)		30 g.

RESTRICTED

Orlando Number	Name and Structure	Repellent Time		Acute Toxicity	Amount Submitted
		Aedes	Anopheles		
6378	$C_6H_5CO_2CH_2CH_2CH_2OH$	7 (302)	8 (44)		325 g.
	1,3-Propanediol, monobenzoate	4 (259/312=0.83)	4 (52/58=0.90)		
6627	$C_2H_5CO_2(CH_2)_4OH$	4 (154)	4 (45)		30 g.
	1,4-Butanediol, monovalerate	4 (152/114=1.33)	4 (45/43=1.05)		
6317	$CH_3CH_2CO_2(CH_2)_5OH$	8 (216)	4 (53)		30 g.
	1,5-Pentanediol, monopropionate	4 (213/240=0.89)	4 (33/39=0.85)		
6987	$C_6H_5CO_2(CH_2)_5OH$	9 (262)	9 (32)		30 g.
	1,5-Pentanediol, monocanthate	4 (234/224=1.04)	4 (30/48=0.63)		
6254	$CH_3CH_2CO_2$ 	31 (250)	31 (59)		50 g.
	1,3-Cyclohexanediol, monopropionate	4 (363/198=1.83)	4 (128/193=0.66)	C	
6257	$C_3H_7CO_2$ 	8 (267)	8 (67)		30 g.
	1,3-Cyclohexanediol, monobutyrate	4 (250/214=1.17)	4 (41/85=0.48)		
6602	$CH_3CH_2CO_2$ 	10 (311)	10 (46)		50 g.
	1,4-Cyclohexanediol, monopropionate	4 (304/278=1.10)	4 (45/53=0.85)		
6526	$CH_3CH_2CO_2CH_2CHOH.C_6H_5$	10 (237)	10 (43)		15 g.
	1,2-Ethanediol, 1-phenyl-, 2-propionate	4 (263/137=1.92)	4 (39/45=0.87)		

RESTRICTED

RESTRICTED

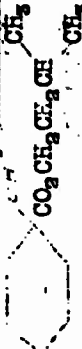
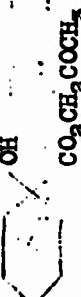
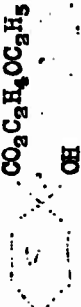
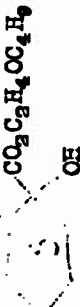
18.

RESTRICTED

19.

Orlando Number	Name and Structure	Aedes	Repellent Time Anopholes	Acute Toxicity	Amount Submitted
6145	$C_6H_{13}CHOHCC_2-C_4H_9$	8 (203)	10 (92)		
	Caprylic acid, 2-hydroxy-, butyl ester	4(223/293=0.76)	4(95/144=0.66)		30 g.
6499	$CH_3CO_2CH_2-C(OH)(CH_3)CC_2C_5H_{11}$ (1)	8 (283)	8 (62)		
	Isobutyric acid, -acetoxy- χ - hydroxy-, isoamyl ester	4(206/230=0.90)	4(47/60=0.78)		15 g.
6551	$CH_3CO_2CH_2-C(OH)(CH_3)CO_2C_6H_{11}$	7 (292)	7 (48)		
	Isobutyric acid, -acetoxy- χ - hydroxy-, cyclohexyl ester	3(401/295=1.36)	3(43/52=0.83)		15 g.
6199	$CO_2C_5H_9$ 	6 (237)	6 (66)		
	Cyclopentane carboxylic acid, 1-hydroxy-, cyclopentyl ester	2(163/186=0.88)	2(64/136=0.47)		30 g.
6198	$CO_2C_6H_{11}$ 	10 (236)	10 (39)		
	Cyclopentanecarboxylic acid, 1- hydroxy-, cyclohexyl ester	4(294/220=1.34) 2(177/73=2.42)	4(60/289=0.21) 2(41/46=0.89)		130 g.
6500	$CC_2C_2H_4CC_4H_9$ 	8 (267)	8 (38)		
	Cyclopentanecarboxylic acid, 1- hydroxy-, 2-butoxyethyl ester	4(335/210=1.60)	4(40/46=0.87)		530 g.

RESTRICTED

Orlando Number	Name and Structure	Repellent Time Aedes	Anopheles	Acute Toxicity	Amount Submitted
6136	 Cyclohexanecarboxylic acid, 1- hydroxy-, isomyl ester	6 (194)	0 (35)		30 g.
6133	 Cyclohexanecarboxylic acid, 1- hydroxy-, cyclopentyl ester	24 (236)	26 (33)		30 g.
6134	 Cyclohexanecarboxylic acid, 1- hydroxy-, cyclohexyl ester	2 (428/371=1.15) 4 (246/238=1.03)	2 (54/240=0.22) 4 (32/91=0.35)	P	4550 g.
6608	 Cyclohexanecarboxylic acid, 1- hydroxy-, acetyl ester	3 (273/323=0.85) 10 (255)	3 (141/253=0.56) 10 (46)		30 g.
6494	 Cyclohexanecarboxylic acid, 1- hydroxy-, 2-ethoxyethyl ester	4 (243/219=1.11) 10 (227)	4 (44/50=0.88) 10 (43)		30 g.
6498	 Cyclohexanecarboxylic acid, 1- hydroxy-, 2-butoxyethyl ester	4 (266/234=1.14) 10 (317)	4 (46/54=0.82) 10 (53)		30 g.
		4 (349/211=1.65)	4 (388/286=1.36)		530 g.

RESTRICTED

20.

RESTRICTED

Orlando Number	Name and Structure	Repellent Time		Acute Toxicity	Amount Submitted
		Aedes	Anopheles		
6596	 Cyclopentanecarboxylic acid, 1-hydroxy-, cyclohexyl ester	6 (330)	6 (50)		15 g.
6601	 Cyclohexanecarboxylic acid, 1-hydroxy-, ethyl ester	7 (244)	5 (32)		30 g.
6625	 Cyclohexanecarboxylic acid, 1-hydroxy-, propyl ester	10 (238)	8 (41)		30 g.
6626	 Cyclohexanecarboxylic acid, 1-hydroxy-, butyl ester	22 (255)	20 (46)	C	30 g.
6599	 Cyclohexanecarboxylic acid, 1-hydroxy-, isomyl ester	4 (203/399=0.76)	4 (38/177=0.21)		540 g.
6600	 Cyclohexanecarboxylic acid, 1-hydroxy-, cyclopentyl ester	10 (271)	10 (39)		30 g.
		4 (274/241=1.14)	4 (36/44=0.82)		15 g.

RESTRICTED

RESTRICTED

21.

RESTRICTED

Orlando Number	Name and Structure	Ados	Repellent Time	Anopholes	Acute Toxicity	Amount Submitted
6220	$C_6H_5CHCHCF_3CO_2 \cdot CH_3$ Hydraerylic acid, -phenyl-, methyl ester	16 (292)	14 (36)	4(28/153=C.18) 2(86/91=C.95)	NP	550 g.
6216	$C_6H_5CHOCHCH_3CO_2 \cdot C_2F_5$ Hydraerylic acid, -phenyl-, ethyl ester	33 (26d)	31 (39)	4(405/229=1.77) 4(413/122=0.35)		5.1 l.
6218	$C_6H_5CHCHCH_2CO_2C_2H_5$ Hydraerylic acid, -phenyl-, propyl ester	12 (284)	10 (36)	4(299/278=1.08) 4(27/110=0.24)		50 g.
6217	$C_6H_5CHOCHCH_2CO_2 \cdot CH(CH_3)_3$ Hydraerylic acid, -phenyl-, isopropyl ester	20 (344)	13 (37)	4(470/366=1.28) 4(50/131=0.38)	G	550 g.
6221	$C_6H_5C(CH_3)OH \cdot CH_2CO_2C_2H_5$ Hydraerylic acid, -methyl-, 2-phenyl-, ethyl ester	9 (209)	6 (36)	4(233/319=0.73) 4(38/167=0.23)		30 g.
6224	$C_6H_5C(CH_3)OH \cdot C_2H_5CO_2CH(CH_3)_3$ Hydraerylic acid, -methyl-, -phenyl-, isopropyl ester	8 (352)	6 (47)	4(317/409=0.78) 4(54/129=0.42)		30 g.
6501	$C_6H_5CHCHCH_2CO_2C_2H_5$ Ethanol, 2-ethoxy-1-phenyl-	10 (157)	8 (42)	3(192/158=1.21) 4(39/53=0.74)		30 g.
5503	$CH_3C_2H_4CH_2CO_2CH_2CH_2CH_2OH$ Ethanol, 1-phenyl-2-propoxy-	14 (262)	14 (57)	4(306/242=1.26) 4(46/60=0.77)		550 g.

23.

RESTRICTED

RESTRICTED

Orlando Number	Name and Structure	Repellent Time		Acute Toxicity	Amount Submitted
		Aedes	Anopheles		
6210	$C_5H_{11}COCHOHC_5H_{11}$ 6-Dodecanone, 7-hydroxy	12 (234)	10 (93)		
6207	$N(CO_2C_2F_5)_3$ Carbamic acid, N,N-dicarboxy-, triethyl ester	9 (194)	7 (71)		550 g.
6166	$(C_2F_5)_2NCOCH_2CF_2CO_2C_2H_5$ Succinamic acid, N,N-diethyl-, ethyl ester	10 (247)	12 (46)		30 g.
6168	$(C_2F_5)_3NCOCH_2CH_2CO_2C_3H_7$ Succinamic acid, N,N-diethyl-, propyl ester	45 (222)	47 (76)	P	60 g.
6172	$(C_2F_5)_2NCOCH_2CH_2CO_2CH(CH_3)_3$ Succinamic acid, N,N-diethyl-, isopropyl ester	9 (255)	10 (72)		5.6 kg.
6288	$(C_2F_5)_2NCOCH_2CH_2CO_2CH(CF_3)CH_2CH_3$ Succinamic acid, N,N-diethyl-, sec-butyl ester	5 (239/280=1.03)	5 (62/165=0.37)		40 g.
6246	$C_5H_{10}NCOCH_2CH_2CO_2C_3H_7$ Succinamic acid, N,N-pentamethylene-, propyl ester	9 (377)	10 (50)		25 g.
		4 (423/338=1.25)	4 (64/93=0.69)		
		8 (247)	8 (69)		
		4 (236/334=0.71)	4 (39/214=0.42)		20 g.

RESTRICTED

Orlando Number	Name and Structure	Repellent Time		Acut Toxicity	Amount Submitted
		Aedes	Anopheles		
6328	$C_5H_9O_2NCOCH_2CH_2CO_2CH(CF_3)_2$ Succinamic acid, N,N-pentamethylene- isopropyl ester	12 (193)	12 (74)		25 g.
6252	$(C_3H_7)_2NCOCH_2CH_2CO_2C_2H_5$ Succinamic acid, N,N-dipropyl- ethyl ester	4C (207)	4C (49)		
6251	$(C_3H_7)_2NCOCH_2CH_2CO_2C_2H_5$ Succinamic acid, N,N-dipropyl- propyl ester	4 (204/213=0.97)	4 (73/153=0.48)	P	4.8 kg.
6393	$(C_3H_7)_2NCOCH_2CH_2CO_2CH(CF_3)CH_3$ Succinamic acid, N,N-dipropyl- sec-butyl ester	8 (318)	8 (41)		50 g.
6343	$(CF_3)_2CHNCOCH_2CH_2CO_2C_3H_7$ Succinamic acid, N,N-diisopropyl- propyl ester	8 (341)	8 (38)		25 g.
635C	$(CF_3)_2CHNCOCH_2CH_2CO_2CH(CF_3)_2$ Succinamic acid, N,N-diisopropyl- isopropyl ester	4 (371/322=1.15)	4 (45/67=0.67)		25 g.
639C	$(CH_3)_2CFNCOCH_2CH_2CO_2CH(CF_3)CH_3$ Succinamic acid, N,N-diisopropyl- sec-butyl ester	11 (310)	12 (39)		25 g.
		4 (323/267=1.21)	4 (40/46=0.87)		
		12 (257)	12 (64)		
		6 (234/228=1.05)	6 (87/76=1.14)		25 g.

RESTRICTED

24.

RESTRICTED

Orlando Number	Name and Structure	Repellent Time		Acute Toxicity	Amount Submitted
		Aedes	Anopheles		
6335	$(C_2H_5)_2NCOCH=CHCO_2C_2H_5$ Maleamic (Fumaramic?) acid, N,N-diethyl-, ethyl ester	8 (261)	8 (51) 4 (239/283=1.02) 4 (61/54=1.13)		15 g.
6336	$C_5H_{10}NCOCH=CHCO_2C_2H_5$ Maleamic (Fumaramic?) acid, N,N-pentamethylene-, ethyl ester	5 (268)	5 (35) 1 (309/317=0.95) 1 (40/52=0.77)		10 g.
6369	$(C_2H_5)_2NCOCH_2CH_2CH_2CO_2C_2H_5$ Glutaramic acid, N,N-diethyl-, methyl ester	8 (300)	8 (47) 4 (226/230=0.95) 4 (53/59=0.90)		25 g.
6373	$(C_3H_7)_2NCOCH_2CH_2CH_2CO_2CF_3$ Glutaramic acid, N,N-dipropyl-, methyl ester	11 (230)	13 (39) 6 (194/121=1.61) 6 (41/72=0.57)		25 g.
6365	$(C_3H_7)_2NCOCH_2CH_2CH_2CO_2C_2H_5$ Glutaramic acid, N,N-dipropyl-, ethyl ester	10 (263)	10 (40) 6 (233/247=0.94) 6 (43/53=0.74)		25 g.
6375	$((CH_3)_2CH)_2NCOCH_2CH_2CH_2CO_2CH_3$ Glutaramic acid, N,N-diisopropyl-, methyl ester	10 (248)	10 (39) 4 (305/275=1.12) 4 (43/61=0.70)		25 g.
6358	$((CH_3)_2CH)_2NCOCH_2CH_2CH_2CO_2C_2F_5$ Glutaramic acid, N,N-diisopropyl-, ethyl ester	15 (239)	16 (37) 6 (262/153=1.71) 6 (36/57=0.63)		25 g.

RESTRICTED

RESTRICTED

RESTRICTED

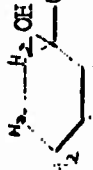
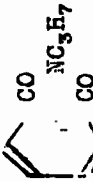
Orlando Number	Name and Structure	Aedes	Repellent Time	Anopheles	Acute Toxicity	Amount Submitted
6397	$((CH_3)_2CH)_2NCOCH_2CH_2CH_2CC_2C_3^{17}$ Glutaric acid, N-N-diisopropyl- propyl ester	8 (244)		8 (36)		
		4(359/229=1.57)		4(39/75=0.52)		525 g.
6511	$(C_2H_5)_2NCOCH_2CH_2CH_2CO_2C_2H_5$ Adipic acid, N,N-diethyl- ethyl ester	8 (276)		8 (50)		
		4(275/253=1.07)		4(58/90=0.65)		32 g.
6484	$((CH_3)_2CH)_2NCOCH_2CH_2CH_2CO_2CH_3$ Adipic acid, N,N-diisopropyl- methyl ester	14 (343)		14 (49)		
		4(381/329=1.16)		4(43/50=0.86)		525 g.
6310	$CF_3CF_2CON(C_4H_9)CH_2CH_2C_2CF_2CF_3$ Propionamide, N-butyl-N- propionoxyethyl-	10 (210)		10 (38)		
		4(202/222=0.91)		4(40/52=0.77)		25 g.
6312	$CH_3CH_2CH_2CON(C_2H_5)CF_2CF_2O_2CCH_2CH_2CH_3$ Butyramide, N-(2-butyroxyethyl)-N- ethyl-	10 (211)		10 (44)		
		4(163/209=0.78)		4(38/62=0.60)		25 g.
6603	$C_4H_9OCH_2CON(C_2H_5)_2$ Acetamide, α -butoxy-N,N-diethyl	10 + d		0 d		
6605	$C_6H_{11}CCl_2CON(C_2H_5)_2$ Acetamide, α -cyclohexoxy-N,N- diethyl-	10 (291)		10 (55)		30 g.
		4(284/199=1.43)		4(42/48=0.88)		28 g.
6461	$CH_3COCH_2CH_2CON(C_3H_7)_2$ Levulinamide, N,N-dipropyl-	9 (206)		9 (40)		
		4(258/227=1.14)		4(34/39=0.87)		20 g.

26.

RESTRICTED

RESTRICTED

27.

Orlando Number	Name and Structure	Repellent Time Aedes	Anopholes	Acute Toxicity	Amount Submitted
6514	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CON}(\text{CH}(\text{CF}_3)_2)_2$	6 (220)	6 (42)		
	Levulinamide, N,N-diisopropyl- OEt	2 (157/191=0.32)	2 (44/59=0.75)		72 g.
6601	$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)\text{CON}(\text{C}_3\text{H}_7)_2$	10 (295)	10 (41)		
	Valeramide, 3-hydroxy-3-methyl- N,N-dipropyl-	4 (294/155=1.89)	4 (37/44=0.84)		19 g.
6563	$\text{CH}_3\text{CH}_2\text{CH}_2\text{-O-CH}_2\text{CON}(\text{C}_2\text{H}_5)_2$	10 + d	0 D		
	Caproamide, N,N-diethyl-3-hydroxy- 3-methyl-				14 g.
6604		10 (277)	10 (41)		
	Cyclohexanecetamide, 1-hydroxy-N,N- diisopropyl-	4 (294/238=1.23)	4 (44/50=0.88)		20 g.
6465		10 + d	0 d.		
	Phthalimide, N-propyl-				25 g.
6544	$\text{CF}_3\text{-CH}_2\text{-CH}_2\text{-NCH}_2\text{CO}_2\text{C}_6\text{H}_{11}$	8 (256)	7 (50)		
	Glycine, N,N-pentamethylene-, cyclohexyl ester	4 (321/227=0.93)	4 (42/50=0.84)		30 g.
6581		8 (212)	4 (43)		
	1-Pyrrolacetic acid, cyclopentyl ester	4 (231/245=0.94)	4 (41/46=0.89)		25 g.

RESTRICTED

RESTRICTED

28.

Orlando Number	Name and Structure	Repellent Time		Acute Toxicity	Amount Submitted
		Aedes	Anopheles		
6545	$ \begin{array}{c} \text{CH}_3\text{CF}_3 \\ \\ \text{C} \begin{array}{l} \diagup \text{NCH}_2\text{CO}_2\text{C}_4\text{H}_9 \\ \diagdown \text{CF}_2\text{CF}_3 \end{array} \\ \\ \text{4-morpholineacetic acid, butyl} \\ \text{ester} \end{array} $	8 (202)	7 (55) 4 (43/52=0.82)		30 g.
6525	$ \begin{array}{c} \text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{FCH}_2\text{CO}_2\text{C}_4\text{H}_9 \\ \text{Glycine, N-benzyl-, butyl ester} \end{array} $	8 (259)	3 (48) 4 (56/78=0.72)		20 g.

RESTRICTED

INSECT REPELLENCY TESTING DATA

A listing has been prepared of all compounds submitted for testing from this laboratory. The compounds are subdivided by functional groups the order of the present card index being followed. The compounds are arranged within the groups into classes of similar types in the order of increasing complexity so that rapid comparison may be made of the data. Liquid compounds were tested against *Aedes aegypti* and *Anopheles quadrimaculatus*; the data are reported as number of tests, total range and average repellency in minutes. Solids and irritant liquids were tested on cotton hose; the values in days to the first bite are recorded.

All candidates were first submitted to the Pure Food and Drug Administration for preliminary irritancy tests. These tests were conducted on the intact skin of rabbits; readings were taken at intervals up to 24 hours. An arbitrary scheme for evaluation, described in reports from that laboratory, was devised in which 4 points was allotted for edema and 4 points for erythema, giving a possible maximum of 8 points to any one compound. The indices, their corresponding irritation significance, and their use recommendations are listed in the following table:

Table VI
Evaluation of Irritation Indices

<u>Score</u>	<u>Irritation</u>	<u>Evaluation</u>
0 - 3	Mild	Passed
3 - 6	Moderate	Failed
6 - 7	Severe	Caution
7 - 8	Severe	Not passed

These tests were begun in October, 1944 and all compounds submitted since that time are reported with an irritation index. Some compounds proved irritant to the test individual at Orlando and are indicated by a I in the appropriate column. The index of refraction and boiling point are included as an aid in establishing the identity and purity of the sample. The numbers under "method of preparation" refer to corresponding sections in the experimental part.

Table VII

Compounds Submitted as Candidate Repellents

Orlando Number	Name	Aedes	Repellent Time	Anopheles	M _D (22°)	b.p. °/mm.	Irrit. Index	Exp. Method
Hydrocarbons								
6522	Hexadecane	2 (27-67)47		2 (25-30)28	1.4944	287/760	4.7	1
6556	1-Hexadecene	2 (21-55)28		2 (23-29)26	1.4410	274/760	3.3	1
6523	Octadecane	2 (44-69)57		2 (44-38)67	1.4391	308/760	5.3	1
6521	1-Octadecene	4 (40-61)52		2 (41-44)43	1.4448	179/15	5.7	1
6161	Bibenzyl	7 d	0 d		m.p. 52.5	107/1		2
6164	1,1-Di phenylethylene	2 (78-130)104		2 (36-49)43		167/38	1	3
615C	Polybenzyl	2 (143-212)178		4 (12-64)32	1.5511	146/1		2
Aldehydes								
6142	β-Isoduraldehyde.	12 (111-193)176		13 (50-226)108	1.5512	92/3		1
Acids								
6287	Crotonic acid	4 d		3 d	m.p. 72°		2.0	1
6171	Butyric acid, γ-ethyl-	13 (41-323)122		12 (29-130)67	1.4131	190/760		1
617C	Znanthic acid	14 (17-311)165		18 (19-332)104		109/9.0	6.3	1
6477	Caprylic acid	0 d			m.p. 15°	1.4273	8.0	1
6117	Endecanoic acid	17 (78-501)318		17 (21-291)115	m.p. 29°	228/160		1

RESTRICTED

31.

Orlando Number	Name	Repellent Time		N _D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6290	Lauric acid	16 d	0 d	m.p. 44°	225/100	5.0	1
6285	Benzole acid	12 d	0 d	m.p. 122°		3.3	1
6541	Hydrocinnamic acid	0 d		m.p. 48°		3.3	1
63C1	Cinnamic acid	1 d	0 d	m.p. 133°	300/760	0.0	1
6253	Succinic acid, monoethyl ester	3 d	2 d	1.4326	113	7.3	4
6242	Succinic acid, monopropyl ester	3 d	2 d	1.4332	104/0.5	8.0	4
6243	Succinic acid, monoisopropyl ester	0 d	0 d	m.p. 51°	93/0.3	7.7	4
6607	Succinic acid, monoallyl ester	0 d	0 d	1.4505	103/0.3	8.0	4
6370	Succinic acid, mono-sec-butyl ester	2(72-74)73	2(15-17)16	1.4315	100/0.25	3.3	4
6391	Succinic acid, mono-(2-methoxyethyl) ester	2(14-54)35	2(16-16)16	1.4436	134/0.3	4.3	4
6343	Glutaric acid, monoethyl ester	2(62-63)63	2(31-32)32	1.4353	84/0.1	4.0	4
6335	Glutaric acid, monopropyl ester	2(68-103)86	2(29-33)31	1.4358	97/0.3	4.7	4
6609	Adipic acid, monopropyl ester	4(57-82)151	4(38-60)42	1.4394	121/0.3	4.0	5
6610	Adipic acid, monoisopropyl ester	2(49-62)56	2(52-65)52	1.4354	108/0.2	3.3	5
6092	Phthalic acid, monohexyl ester	2(15-63)32	2(17-23)20	1.5145			6
6033	Phthalic acid, nonoheptyl ester	0 d	2(16-23)20	1.5071		1.0	6

RESTRICTED

Crlendo Number	Name	Repellent Time		N _D (22°)	b.p. °/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6031	Phthalic acid, monoethyl ester	2(20-34)27	2(21-35)28	1.5164			6
6173	Valeric acid, α -hydroxy-, acetate	0 d	0 d	1.4284	95/0.5	8.0	7
6211	Cyclohexanecarboxylic acid, 1-hydroxy-, acetate	2(32-39)36		m.p. 101°		5.0	7
6231	Acetylsalicylic acid	2 d	0 d	m.p. 134°		0.7	1
6295	Acetic acid, phenoxy-	0 d	0 d	m.p. 99°	285°-(d)	4.7	1
6193	Benzoic acid, α -ethoxy-	2(22-35)22	2(24-36)20	1.5403	129/1.0	3.0	8
6233	Anisic acid	3 d	0 d	m.p. 184°		1.0	1
6304	Levulinic acid	0 d	0 d	m.p. 37°	246/760	6.3	1
6167	Valeric acid, α -hydroxy-	2(23-43)36	4(14-46)20	1.4456		1	9
6302	Cyclohexanecarboxylic acid, 1-hydroxy-	0 d	0 d	m.p. 106°		1.3	9
6296	Salicylic acid	3 d	0 d	m.p. 159°		3.3	1
6293	dl-Mandelic acid	1 d	0 d	m.p. 118°		4.0	1
6300	Benzilic acid	7 d	0 d	m.p. 150°		0.0	1
6239	2-Naphthoic acid, 3-hydroxy	3 d	2 d	m.p. 216°		2.0	1
6234	Anthranilic acid	7 d	0 d	m.p. 145°		2.0	1
6303	Succinamic acid, N,N-diethyl	2 d	0 d	m.p. 85°		0.7	10
6305	4-morpholinebutyric acid, γ -oxo-	2 d	0 d	m.p. 71°		2.3	10

RESTRICTED

Orlando Number	Name	Repellent Time		Anopheles		N_D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
		Aedes							
6288	Hippuric acid	3 d		0 d		m.p. 189°		0.7	1
6297	Succinic acid	1 d		0 d		m.p. 185°	235° (d)	2.0	1
6291	Maleic acid	0 d		0 d		m.p. 130°		4.3	1
6282	Adipic acid	2 d				m.p. 152°		0.7	1
6294	Mucic acid	(Not tested - too insoluble)				m.p. 206° (d)		0.3	1
6299	Azulalic acid	0 d		2 d		m.p. 107°	360 (d)	2.7	1
6292	dl-Malic acid	1 d		0 d		m.p. 128°		2.0	1
6293	d-Tartaric acid	1 d		0 d		m.p. 170°		1.7	1
6286	Citric acid	3 d		0 d		m.p. 153°		1.3	1
6463	Trimesic acid	0 d		0 d		m.p. 375°		1.3	1
6352	Glutaric anhydride	0 d		0 d		m.p. 50°		4.3	11
6132	Caproic anhydride	4(49-207)123		4(6-56)43		1.4267	109/8.0		1
6144	Heptylic anhydride	4(22-257)140		4(6-162)84		1.4321	121/0.5		12
6135	Caprylic anhydride	12(149-469)271		12(28-174)81		1.4364	136/0.5		12
6143	Butyric anhydride, λ -diethyl-	2(30-80)55		4(47-111)66		1.4298	131/30		12
Esters									
6012	Acetic acid, amyl ester	2(8-9)2		2(11-14)13		1.4020	148/76.0		13
626C	Acetic acid, Δ hendecoenyl ester	2(26-33)30		2(36-72)54		1.4378	74/0.02	533	13

33.

RESTRICTED

RESTRICTED

Orlando Number	Name	Repellent Time Aedes	Anopheles	N_D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
6112	Propionic acid, lauryl ester	2(15-16)16	2(17-19)18	1.4322	140/3		13
6111	Propionic acid, octyl ester	2(35-61)48	2(36-60)48	1.4407	165/1		13
6009	Butyric acid, methyl ester	2(25-36)31	2(27-29)28	1.3857	130/760		1
6123	Butyric acid, propyl ester	2(69-106)88	2(11-60)36		143/760		1
6125	Butyric acid, butyl ester	4(8-53)35	4(12-56)42		165/760	1	1
6048	Butyric acid, tert-butyl ester	2(12-16)14	2(16-18)17	1.3981	144/760		14
6124	Butyric acid, amyl ester	2(29-29)29	2(31-32)32		68/15		1
6126	Butyric acid, isoamyl ester	2(42-42)42	2(39-42)41			1	1
6058	Butyric acid, tert-amyl ester	2(13-59)36	2(14-16)15	1.4058	143/760		14
6074	Butyric acid, 2-hexyl ester	2(17-21)19	2(21-24)23	1.4118	100/38		13
6101	Butyric acid, lauryl ester	2(12-35)24	2(9-18)14	1.4348	153/4-5		13
6059	Butyric acid, cyclohexyl ester	2(32-32)32	2(33-33)33	1.4403	116/40		14
6120	Butyric acid, benzyl ester	2(64-106)85	2(55-68)62		109/9		1
6152	Butyric acid, 3-phenylpropyl ester	18(79-461)186	17(28-280)61	1.4871 •	91/0-2		13
6121	Isobutyric acid, ethyl ester	2(23-45)24	2(26-46)26		110/760		1
6018	Isobutyric acid, propyl ester	2(28-28)28	2(31-31)31	1.3939	132/760		13
6122	Isobutyric acid, isobutyl ester	2(26-41)24	2(30-42)36		148/760		1
6017	Isobutyric acid, amyl ester	2(10)		1.4088	107/82		13

34.

RESTRICTED

RESTRICTED

35.

Orlande Number	Name	Repellent Time		n _D (20°)	b.p. ³ /mm.	Irrit. Index	Exp. Method
		Notes	Anapholes				
6019	Isobutyric acid, 2-methyl- butyl ester	2(16)		1.4064	96/70		13
6108	Isobutyric acid, lauryl ester	2(9-50)20	2(49-51)50	1.4315	140/5		13
6029	Isobutyric acid, cyclohexyl ester	2(18-18)18	2(20-20)20	1.4371	64/9	1	13
6003	Crotonic acid, methyl ester	2(4-25)15	2(3-22)13	1.4204	120/760		15
6127	Crotonic acid, propyl ester	0 d	0 d		155/760	1	1
6128	Crotonic acid, isobutyl ester	2(31-31)31	2(33-34)34		171/760		1
6016	Crotonic acid, amyl ester	2(24-24)24	2(27-27)27	1.4346	125/75		13
6010	Crotonic acid, 2-methylbutyl ester	2(21-51)36	2(18-51)35	1.4325	124/90		13
6057	Crotonic acid, octyl ester	2(43-117)80	2(45-54)50	1.4459	135/40		13
6047	Crotonic acid, cyclohexyl ester	4(62-96)83	4(10-36)42	1.4653	127/37		13
6046	Crotonic acid, benzyl ester	6(118)		1.5173	160/40	1	13
6191	Crotonic acid, phenethyl ester	2(67-74)71	2(42-65)54	1.5134	114/1	4.0	13
6192	Crotonic acid, 3-phenylpropyl ester	2(27-31)29	2(21-33)27	1.5098	118/1	4.0	13
6062	Valeric acid, propyl ester	2(21-30)26	2(24-32)28	1.4047	76/40		13
6095	Valeric acid, 2-hexyl ester	3(19-46)22	3(22-43)21	1.4151	115/37		13
6096	Valeric acid, 2-heptyl ester	2(14-72)43	2(15-75)45	1.4192	132/40		13

RESTRICTED

RESTRICTED

36.

Orlando Number	Name	Repellent Time Acetes	Anopheles	ND (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
6060	Valeric acid, 2-octyl ester	2(74-74)74	2(11-75)43	1.4226	145/40		13
6061	Valeric acid, cyclohexyl ester	2(56-59)58	2(16-18)17	1.4427	131/40		13
6079	Isovaleric acid, <u>tert</u> -butyl ester	2(16-20)18	2(20-20)20	1.4000	68/40		14
6045	Isovaleric acid, isoamyl ester	2(17-23)23	2(17-31)24	1.4100	194/760		13
6092	Isovaleric acid, lauryl ester	2(21-97)59	2(23-33)27	1.4341	163/5		13
6014	Caproic acid, propyl ester	2(18-36)27	2(15-33)24	1.4113	94/32		13
6020	Caproic acid, isopropyl ester	2(17)		1.4063	84/30		13
6129	Caproic acid, butyl ester	2(39-40)40	2(15-41)28		204/760		1
6030	Caproic acid, amyl ester	2(22-94)58	2(89-96)93	1.4199	125/40		13
6035	Caproic acid, hexyl ester	2(32-63)48	2(19-34)27	1.4234	143/39		13
6074	Caproic acid, 2-heptyl ester	2(15-71)43	2(16-75)46	1.4226	101/5		13
6038	Caproic acid, octyl ester	2(23-42)33	2(18-69)44	1.4326	105/5		13
6076	Caproic acid, lauryl ester	2(60-74)67	2(11-63)27	1.4374	165/4.5		13
6044	Caproic acid, cyclohexyl ester	2(94-94)94	2(94-95)95	1.4416	145/41		13
6077	Caproic acid, benzyl ester	2(74-147)110	2(22-28)25	1.4360	122/5		13
6105	Caproic acid, cinnamyl ester	3(14-70)37	2(39-49)45	1.5163	163/5		16
6015	Caproic acid, δ -methyl-, amyl ester	2(12-51)32	2(48-74)67	1.4220	155/75		13

RESTRICTED

Orlando Number	Name	Repellent Time		N _D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
		Aedes.	Anopheles				
6331	Palmitic acid, ethyl ester	4(18-70)6C	4(21-73)51	1.4384		4.C	1
6076	Benzoic acid, <u>tert</u> -amyl ester	2(27-72)5C	2(41-73)57	1.4917	90/4		7
6067	Benzoic acid, cyclohexyl ester	2(22-54)38	2(55-79)67	1.5205	97/1		13
605C	Benzoic acid, 2-hexyl ester	4(16-172)91	4(18-126)65	1.4830	97/1		13
6049	Benzoic acid, 4-methyl-2- amyl ester	2(17-39)28	2(20-42)31	1.4870	93/1		13
6027	Benzoic acid, heptyl ester	2(19-20)2C	2(45-54)50	1.4896	110/1		13
6069	Benzoic acid, 2-heptyl ester	2(18-24)26	2(20-36)28	1.4862	104/1		13
6072	Benzoic acid, 5-methyl-2-hexyl ester	2(51-96)74	2(25-53)32	1.4851	103/1		13
607C	Benzoic acid, 2-octyl ester	2(39-84)62	2(42-80)61	1.4829	112/1		13
6324	1-Naphthoic acid, ethyl ester	2(27-41)34	2(29-45)37	1.5934	309/760	1.7	1
6625	Perbenzoic acid, <u>tert</u> -butyl ester	5 d	5 d			7.C	1
Diesters							
6318	Glycol, dibutyrate	4(32-73)5C	4(17-33)25	1.4233	111/5	2.0	1
610C	Glycol, diisobutyrate	2(30-95)88	2(35-35)35	1.4170	87/4.0		13
6102	Glycol, dicaprate	2(93-99)98	2(52-81)68	1.4332	146/5.0		17
6313	Glycol, bis(<u>α</u> -ethylbutyrate)	2(30-30)30	2(33-33)33	1.4299	96/0.2	1.7	13
6321	1,2-Fropanediol, diisobutyrate	2(71-72)72	2(33-35)34	1.4160	64/0.1	1.0	13

RESTRICTED

RESTRICTED

37.

RESTRICTED

38.

Orlando Number	Name	Aedes	Repellent Time	Anopheles	M_D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method.
6346	1,2-Propanediol, divalerate	2(52-82)67	2(26-55)41	1.1269	91/0.1	1.0	13	
6344	1,2-Propanediol, diisovalerate	2(101-102)102	2(62-63)63	1.4234	74/0.1	2.7	13	
6334	1,2-Propanediol, diacaproate	2(32-34)33	2(34-36)35	1.4310		2.7	13	
636C	1,2-Propanediol, bis(α -ethylbutyrate)	2(45-46)46	2(21-48)35	1.4289	95/0.2	2.0	13	
6384	1,3-Propanediol, dipropionate	2(78-78)78	2(25-54)40	1.4231	90/2	0.3	17	
6115	1,3-Propanediol, diisobutyrate	11(28-193)131	15(41-132)22	1.4213	103/5.0		13	
6270	1,3-Propanediol, diacetate	2(51-70)60	2(20-24)22	1.4671	132/4.0	5.0	13	
6401	1,3-Propanediol, divalerate	2(13-21)20	2(22-22)23	1.4312	113/1.0	2.3	13	
6106	1,3-Propanediol, diacaproate	2(9-151)70	4(16-62)32	1.4349	159/5.0		17	
6417	1,3-Propanediol, bis(α -ethylbutyrate)	2(11-12)12	2(15-41)28	1.4321	114/1.0	3.7	13	
6261	1,3-Propanediol, dibenzoate	2(20-34)27	2(23-38)31	m.p. 57°		1.3	7	
6322	1,4-Butanediol, diacetate	2(59-67)63	2(27-36)32	1.4225	72/0.1	1.0	17	
6326	1,4-Butanediol, dipropionate	2(36-112)74	2(38-55)47	1.4265	73/0.2	1.0	17	
6330	1,4-Butanediol, dibutyrate	2(27-59)43	2(33-56)44	1.4300	99/0.2	0.7	17	
6329	1,4-Butanediol, diisobutyrate	2(28-30)54	2(33-51)41	1.4251	87/0.2	0.0	13	
6323	1,4-Butanediol, divalerate	2(30-69)50	2(33-33)33	1.4336	119/0.2	0.7	13	
6366	1,4-Butanediol, bis(methoxyacetate)	2(22-37)30	2(20-21)21	1.4394	121/0.2	0.7	13	

RESTRICTED

Orlando Number	Name	Repellent Time		n _D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6341	1,4-Butanediol, bis(α -ethylbutyrate)	>(44-86)65	2(30-47)32	1.4342	121/0.1	4.0	13
6407	1,5-Pentanediol, diformate	2(49-78)64	2(53-81)67	1.4278	121/17	1.7	18
6263	1,5-Pentanediol, diaacetate	22(36-291)167	22(30-204)81	1.4258	76/0.2	2.7	13
6154	1,5-Pentanediol, dipropionate	27(23-404)170	31(24-281)98	1.4290	92/0.4	4.8	13
6153	1,5-Pentanediol, dibutyrate	6(86-289)153	10(29-150)24	1.4314	130/1.0		13
6276	1,5-Pentanediol, diisobutyrate	6(7-137)62	6(11-99)51	1.4280	98/0.3	3.7	13
6274	1,5-Pentanediol, diacetate	2(22-35)29	2(23-36)30	1.4674	126/0.2	4.0	13
6266	1,5-Pentanediol, divalerate	2(18-54)36	2(21-23)22	1.4354	127/0.2	2.3	13
6155	1,5-Pentanediol, diisovalerate	8(107-400)161	11(34-140)55	1.4317	155/4.0		13
6383	1,5-Pentanediol, dipivalate	8(83-319)259	8(25-84)65	1.4280	90/0.2	0.7	7
6353	1,5-Pentanediol, diacaproate	2(25-26)26	2(28-28)28	1.4389	132/0.1	2.3	13
6379	1,5-Pentanediol, bis(methoxyacetate)	2(53-90)72	2(30-30)30	1.4406	127/0.2	0.7	13
6268	1,5-Pentanediol, bis(α -ethylbutyrate)	6(16-70)40	6(20-73)36	1.4359	138/0.2	1.8	13
6394	1,5-Pentanediol, diacanthate	2(13-19)19	2(21-22)22	1.4415	154/0.2	3.3	7
6278	1,5-Pentanediol, dibenzozate	2(14-28)21	2(17-30)24	m.p. < 37°		3.7	13
630C	1,6-Hexanediol, diformate	2(83-101)92	2(63-71)67	1.4299	91/2.0	1.0	18
6316	1,6-Hexanediol, diaacetate	8(193-313)243	7(74-317)148	1.4285	97/1	1.7	17

EXPERIMENT

Orlando Number	Name	Repellent Time Aedes	Anopheles	n _D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
6319	1,6-Hexanediol, dipropionate	12(30-302)153	12(33-324)102	1.4317	117/1.0	1.0	17
6377	1,6-Hexanediol, dibutyrate	2(69-97)85	2(11-12)12	1.4341	128/2.0	2.7	17
6595	1,9-Nonanediol, diformate	2(19-76)48	2(19-22)21	1.4371	107/0.4	0.7	18
6337	1,9-Nonanediol, diacetate	10(84-450)225	8(21-212)62	1.4351	107/0.2	1.3	17
6349	1,9-Nonanediol, dipropionate	2(13-56)35	2(15-20)18	1.4374	119/0.1	1.0	17
6197	1,10-Decanediol, diacetate	0 d	0 d	m.p. <37°			1
6110	Diethylene glycol, dipropionate	4(79-267)150	4(26-270)22	1.4295	118/2.0		13
6562	Diethylene glycol, bis(ethyl carbonate)	2(18-47)22	2(22-49)36	1.4293	109/0.3	2.0	19
6597	Diethylene glycol bis(propyl carbonate)	2(61-121)21	2(15-62)32	1.4328	129/0.3	2.0	19
6564	Diethylene glycol bis(isopropyl carbonate)	5(70-121)105	5(48-137)86	1.4278	118/0.2	1.3	19
6593	Diethylene glycol bis(isobutyl carbonate)	2(61-88)75	2(51-64)58	1.4326	142/0.3	4.0	19
6631	Diethylene glycol, bis(phenyl carbonate)			m.p. 40° (lit.)			1
6425	1,2-Cyclohexanediol, diacetate	2(15-94)55	2(13-46)22	1.4472	60/0.1	3.0	17
6426	1,2-Cyclohexanediol, dipropionate	2(20-20)20	2(23-23)23	1.4461	75/0.1	1.0	17
6428	1,2-Cyclohexanediol, dibutyrate	2(20-74)47	2(21-23)22	1.4472	86/0.1	1.3	17

Orlando Number	Name	Repellent Time		N _D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6435	1,2-Cyclohexanediol, diisobutyrate	2(76-109)23	2(24-53)32	1.4501	70/0.1	1.7	13
6236	1,3-Cyclohexanediol, diacetate	8(138-274)216	6(30-114)72	1.4494	83/0.2		17
6237	1,3-Cyclohexanediol, dipropionate	6(74-221)138 2(123/170)	4(32-194)77 2(39/44)	1.4483	94/0.2		13
6235	1,3-Cyclohexanediol, bis(ethyl carbonate)	2(52-52)52		1.4483	124/0.2		7
6238	1,2-Cyclohexanediol, 5,5-dimethyl-, diacetate	2(25-29)27	2(29-33)31	1.4472	82/0.2	3.7	17
6422	1,4-Cyclohexanediol, diacetate	1 d	1 d	m.p. 85-90°		1.0	17
6424	1,4-Cyclohexanediol, dipropionate	1 d	0 d	m.p. 65-70°		2.7	17
6438	1,4-Cyclohexanediol, diisobutyrate	2(21-21)21	2(25-25)25	1.4436	96/0.2	2.0	13
6421	Catechol, dipropionate	2(25-53)42	2(28-28)28	1.4989	100/0.3	2.1	20
6492	Catechol, dibutyrate	0 d	0 d	1.4844	125/0.25	7.0	20
6314	Resorcinol, diacetate	2(36-112)74	2(38-38)38	1.5031	103/0.2	1.0	20
6415	Resorcinol, acetate propionate	2(16-19)18	2(20-21)21	1.4960	117/0.2	2.3	7
6339	Resorcinol, dipropionate	4(55-81)64	4(21-32)27	1.4968	111/0.2	2.7	20
6357	Resorcinol, dibutyrate	2(14-53)34	2(15-18)17	1.4885	116/0.1	1.0	7
6338	Hydroquinone, dipropionate	0 d	0 d	m.p. 111-113°		0.3	20

RESTRICTED

TABLE 10

Crlando Number	Name	Repellent Time		n _D (22°)	b.p. °/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6179	Carbonic acid, benzyl ethyl ester	2(46-83)55	2(20-86)53	1.4896	74/0.5	6.0	7
6176	Carbonic acid, ethyl phenethyl ester	8(84-172)132 4(139/203)	8(42-132)21 4(82/156)	1.4884	82/0.5	5.3	7
6175	Carbonic acid, ethyl 3-phenylpropyl ester	2(27-88)53		1.4871	94/0.5	3.0	7
6180	Carbonic acid, cinnamyl ethyl ester	2(16-50)23	2(16-16)16	1.5255	109/0.5	5.3	7
6186	Carbonic acid, 4-tert-amylcyclohexyl ethyl ester	2(50-102)76	2(53-103)78	1.4557	96/0.5	7.0	7
6177	Carbonic acid, ethyl p-methoxybenzyl ester	2(33-75)54	2(24-31)28	1.5009	103/0.5	7.3	7
6190	Carbonic acid, 2-(3-carbethoxy)hexyl ethyl ester	2(61-74)68	2(63-74)69	1.4240	86/1.0	2.3	7
6205	Carbonic acid, 2-(3-carbethoxy)octyl ethyl ester	2(6-34)20		1.4281	113/1.0	2.0	7
6629	Carbonic acid, di-m-tolyl ester	2(33-93)63	2(30-30)30	m.p. 30-35°	129/0.2	5.7	21
6626	Carbonic acid, di-p-tolyl ester	0 d	0 d	m.p. 110-111°			21
6630	Carbonic acid, ditolyl ester (m and p)	2(20-55)38	2(19-23)21		127/0.2	4.7	21
6011	Oxalic acid, dibutyl ester	0 d	0 d	1.4211	118/0.1	1	1
6013	Oxalic acid, diisooamyl ester	0 d	0 d		137/0.15	1	1

Orlando Number	Name	Repellent Time		n _D (20°)	b.p.°/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6036	Malonic acid, isopropyl-, diethyl ester	2 (60-89) 75	2 (13-18) 16	1.4441	106/30		1
6356	Malonic acid, butyl-, diethyl ester	2 (14-55) 35	2 (16-17) 17	1.4216	109/10	1.3	2
6354	Malonic acid, ethylisopropyl-, diethyl ester	2 (64-65) 65	2 (30-67) 42	1.4289		2.3	1
6355	Malonic acid, butylethyl-, diethyl ester	8 (9-367) 141	8 (11-97) 41	1.4294		1.7	1
6063	Succinic acid, diamyl ester	4 (16-147) 67	4 (4-31) 22	1.4346	122/1.0	1	13
6055	Succinic acid, di-2-pentyl ester	2 (19-73) 46	2 (22-23) 23	1.4292	107/1.0		13
6064	Succinic acid, di-3-pentyl ester	2 (57-78) 68	2 (48-62) 55	1.4290	106/1.0		13
6059	Succinic acid, bis(2-methyl-1- butyl) ester	2 (32-32) 32	2 (33-33) 33	1.4326	117/1.0		13
6053	Succinic acid, bis(4-penten-1-yl) ester	2 (35-64) 50	2 (16-37) 27	1.4521	127/1.0		13
6054	Succinic acid, dicyclopentyl ester	2 (44-99) 17	2 (29-56) 43	1.4664	137/1.0		13
6585	Fumaric acid, diallyl ester	0 d	0 d	1.4686	97/3.0	0.7	13
6026	Glutaric acid, dimethyl ester	2 (69-69) 62	2 (28-70) 42	1.4250	113/30		1
6007	Glutaric acid, diethyl ester	2 (45-55) 50	2 (24-49) 67	1.4223	69/1.0		1
6023	Glutaric acid, dipropyl ester	2 (17-99) 53	2 (19-20) 20	1.4268	97/2.0		22

REPRODUCED

REPRODUCED

Orlando Number	Name	Repellent Time Aedes	Anopheles	n_D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
6041	Glutaric acid, diisopropyl ester	6(90-206)150 2(149/210)	6(29-147)52 2(34/45)	1.4203	71/1.0		22
6043	Glutaric acid, dibutyl ester	6(19-250)135 2(120/123)	6-22-159)61 2(41/47)	1.4312	112/1.0		22
6024	Glutaric acid, diisobutyl ester	2(29-96)63	2(32-36)34	1.4276	92/1.0		22
6051	Glutaric acid, bis(2-methyl-1-butyl) ester	2(61-62)62	2(17-63)40	1.4340	133/1.0		22
6552	Glutaric acid, α -hydroxy- α -methyl- γ -lactone, propyl ester	4(99-269)157	4(53-68)57	1.4406	96/0.5	2.0	23
6052	Adipic acid, dipropyl ester	4(106-174)137	2(47-107)77	1.4297	110/1.0	I	13
6066	Adipic acid, diisopropyl ester	10(79-234)150 4(121/176)	10(14-146)52 4(32/41)	1.4233	96/1.0		13
6065	Adipic acid, diallyl ester	15(30-263)110	22(38-63)52	1.4567	111/1.0	I	13
6021	Suberic acid, diethyl ester	2(100-137)119	2(25-37)31	1.4316	126/2		1
6080	Azelallic acid, dimethyl ester	3(19-170)75	3(21-51)37	1.4342	104/1.0	I	24
6279	Azelallic acid, diethyl ester	2(41-77)52	2(14-44)22	1.4328	116/0.4	3.0	13
6071	Azelallic acid, dipropyl ester	4(53-89)65	4(38-122)70	1.4359	135/1.0		19
6081	Azelallic acid, diisopropyl ester	2(12-57)35	2(14-59)37	1.4305	120/1.0		19
6039	Phthalic acid, diisobutyl ester	8(19-60)40	8(23-63)32	1.4336	153/3.0		13

RETRACTED

44.

RETRACTED

Orlando Number	Name	Repellent Time Aedes	Anopheles	n_D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
6040	Phthalic acid, di- <u>sec</u> -butyl ester	2(7-54)31	2(7-3)8	1.4883	129/1.0		13
6159	Phthalic acid, hexyl methyl ester	4(21-105)50	4(18-37)28	1.4960	149/1.0	-	25
6160	Phthalic acid, methyl octyl ester	2(47-47)47	6(16-93)28	1.4960	143/0.5		25
6467	Pyromellitic acid, tetramethyl ester	0 d	0 d	m.p. 134-136°		1.7	1
6195	Butyric acid, β -acetoxy-, α -ethyl-, ethyl ester	2(30-30)30	2(32-32)32	1.4197	113/30	2.7	7
6496	Cyclopentanecarboxylic acid, 1-acetoxy-, tetrahydrofurfuryl ester	10(113-442)304	8(38-56)48	1.4654	127/0.5	1.0	7
6420	Cyclohexanecarboxylic acid, 1-acetoxy-, tetrahydrofurfuryl ester	2(49-84)67	2(25-29)27	1.4749	123/0.5	1.3	7
6448	Cyclohexanecarboxylic acid, 1-propionyloxy-, propyl ester	2(70-71)71	2(14-44)29	1.4482	93/0.5	2.7	7
6449	Cyclohexanecarboxylic acid, 1-butyroxy-, propyl ester	2(21-21)21	2(22-24)23	1.4492	99/0.5	2.0	7
Ether-Esters							
6113	Propionic acid, p-methoxy-benzyl ester	13(81-452)234	13(15-137)53	1.5143	116/2.5		16
6118	Butyric acid, p-methoxy-benzyl ester	4(17-234)137	4(21-39)53	1.5006	133/3		16

RESTRICTED

RESTRICTED

Orlando Number	Name	Repellent Time Aedes	anopheles	MD (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
6169	Caproic acid, tetrahydro- furfuryl ester	9(134-264)212	11(17-259)127		142/19		1
6104	Caproic acid, p-methoxybenzyl ester	4(36-163)100 2(53/116)	4(15-42)21 2(33/38)	1.4943	162/5		16
6022	Benzoic acid, tetrahydro- furfuryl ester	21(273)	2(15-15)15	1.5204	120/1		13
6307	Anisic acid, methyl ester	20 + d	2 d	m.p. 43°	256/760	0.0	1
6099	Anisic acid, isopropyl ester	5(17-345)198	5(19-133)63	1.5119	117/3		13
6075	Anisic acid, propyl ester	2(65-128)27	2(10-19)15	1.5166	130/5		13
6073	Anisic acid, butyl ester	13(25-267)90 O d	18(25-64)41	1.5130	144/4	NP	13
6107	Anisic acid, isobutyl ester	2(79-108)94	2(47-53)52	1.5101	132/3		13
6091	Anisic acid, amyl ester	2(49-54)52	2(50-56)53	1.5102	144/3		13
6109	Furoic acid, furfuryl ester	8(13-444)178	10(11-62)32	1.5262	121/1.5		26
6156	2-Furanaacrylic acid, butyl ester	4(80-142)114	4(8-151)89	1.5312	120/1		13
6157	2-Furanaacrylic acid, propyl ester	10(107-283)175 2(131/200)	9(11-204)90 2(47/52)	1.5382	106/1		13
6151	Vanillic acid, ethyl ester	4(100-255)149	6(15-21)19	1.5457			27
6368	1,3-Dioxolane-2-acetic acid, 2-methyl-, ethyl ester	2(36-46)41	2(20-40)30	1.4310	53/0.2	1.0	28
6440	1,3-Dioxolane-2-acetic acid, 2-methyl-, cyclohexyl ester	6(71-235)131	8(17-47)32	1.4593	88/2	1.7	28

RESTRICTED

RESTRICTED

Orlando Number	Name	Repellent Time		n _D (20°)	b.p.°/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6372	1,3-Dioxolane-2-acetic acid, 2-methyl-, benzyl ester	2(36-46)41	2(19-19)19	1.5055	124/0.1	0.0	23
6381	1,3-Dioxolane-2-propionic acid, 2-methyl-, cyclohexyl ester	2(62-63)63	2(29-29)29	1.4622	106/0.2	1.3	28
6502	1,3-Dioxolane-2-propionic acid, 4-methoxyethyl-2-methyl-, ethyl ester	10(52-53)247	3(34-55)46	1.4376	86/0.2	1.7	28
6430	1,3-Dioxolane-2,2-diacetic acid, diethyl ester	2(42-56)42	2(22-46)24	1.4452	107/0.4	1.7	28
6250	1,3-Dioxolane-4,5-dicarboxylic acid, 2,2-dimethyl-, diethyl ester	2(31-38)35	2(25-52)22	1.4338	88/0.4	2.3	29
6548	1,3-Dioxolane-4,5-dicarboxylic acid, 2-ethyl-2-methyl-, dimethyl ester	2(52-79)66	2(25-25)25	1.4398	85/0.1	0.7	28
6571	1,3-Dioxolane-4,5-dicarboxylic acid, 2-methyl-2-propyl-, dimethyl ester	3(59-98)83	3(8-34)25	1.4401	85/0.2	1.7	28
6460	1,3-Dioxolane-4,5-dicarboxylic acid, 2-isobutenyl-2-methyl-, dimethyl ester	2(21-54)28	2(24-24)24	1.4585	93/0.3	1.0	28
6462	1,3-Dioxolane-4,5-dicarboxylic acid, 2-isobutyl-2-methyl-, dimethyl ester	2(44-45)45	2(45-48)47	1.4413	80/0.15	0.7	28
6238	1,3-Dioxolane-4-one, 2,2-dimethyl-5-phenyl	21 + d	3 d	m.p. 48°	85/0.3	1.7	29

RESTRICTED

47.

RESTRICTED

Orlando Number	Name	Repellent Time Aedes	anopheles	MD (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
653C	1,3-Dioxolan-4-one, 2-ethyl- 2-methyl-5-phenyl-	2(43-48)66, 4d	2(49-49)49	1.5045	92/0.3	0.3	28
6546	1,3-Dioxolan-4-one, 2-methyl- 5-phenyl-3-propyl-	2(26-31)52	2(31-50)41	1.5011	39/0.1	0.7	28
624C	1,3-Dioxolane-2-acetic acid, 2-methyl-4-oxo-5-phenyl-, methyl ester	2(27-28)28	2(30-30)30	1.5072	134/0.5	3.7	28
6414	1,3-Benzodioxole-2-acetic acid, 2-methyl-, ethyl ester	4(52-222)157	4(25-69)47	1.5152	37/0.2	2.0	28
6413	1,3-Benzodioxole-2-propionic acid, 2-methyl-, ethyl ester	2(43-45)44	2(17-18)13	1.5047	105/0.2	2.3	28
6272	1,3-Dioxane-2-acetic acid, 2-methyl-, ethyl ester	2(70-72)71	2(21-21)21	1.4417	113/16	4.0	28
655C	1,3-Dioxaspiro(4.4)nonane-2- carboxylic acid, 2-methyl-4- ethyl ester	2(56-112)84	2(27-29)28	1.4480	92/0.5	1.7	28
6212	1,3-Dioxaspiro(4.5)decan-4- one, 2,2-dimethyl-	2(44-64)54		1.4506	103/15		29
6427	1,3-Dioxaspiro(4.5)decan-2- carboxylic acid, 2-methyl- 4-oxo-, ethyl ester	2(23-51)27	2(26-26)26	1.4535	91/0.3	2.3	28
6474	1,3-Dioxaspiro(4.5)decan-2- carboxylic, 2-methyl-4-oxo-, propyl ester	2(48-51)50	2(53-54)54	1.4538	89/0.1	2.7	28
6215	1,3-Dioxaspiro(4.5)decan-2- acetic acid, 2-methyl-4-oxo-, ethyl ester	4(101-252)172	2(32-32)32	1.4630	107/0.5		28

RESTRICTED

RESTRICTED

Orlando numb.r	Name	Aedes	Repellent Time Anopheles	n_D (22°)	b.p. °/mm.	Irrit. Exp. Index Method
6423	1,3-Dioxaspiro(4.5)decano-2-methanol, 2-methyl-4-oxo-, acetate	2(14-51)33	2(17-21)12	1.4593	101/0.3	2.3 28
6547	1,4-Dioxaspiro(4.4)nonan-2-one, 3-phenyl	0 d	0 d	m.p. 64-65°		3.0 28
6434	1,4-Dioxaspiro(4.4)nonane-6-carboxylic acid, ethyl ester	2(24-75)50	2(24-25)25	1.4553	89/1	2.0 28
6306	1,4-Dioxaspiro(4.4)nonane-2,3-dicarboxylic acid, dimethyl ester	2(9-52)21	2(12-12)12	1.4610	107/0.5	3.7 28
6439	1,4-Dioxaspiro(4.4)nonane-2,3-dicarboxylic acid, diethyl ester	2(22-51)27	2(20-23)22	1.4552	101/0.2	1.7 28
6244	1,4-Dioxaspiro(4.5)decan-2-one, 3-phenyl-	0 d	0 d	m.p. 102°		2.3 28
6441	1,4-Dioxaspiro(4.5)decano-2,3-dicarboxylic acid, dimethyl ester	4(9-110)71	4(11-46)28	1.4717	98/0.2	0.7 28
6213	7,15-Dioxadispiro(5.2.5.1)pentadecan-8-one	2(50-113)82		1.4854	91/0.5	28
Keto-Esters						
6579	Benzoic acid, acetonyl ester	10 + d				
6593	α -Toluic acid, acetonyl ester	2(46-48)47	2(21-49)35	1.5106	96/0.2	2.0 30
6507	Pyruvic acid, 2-ethylbutyl ester	2(34-34)34	2(37-38)28	1.4250	63/0.3	1.7 31

RESTRICTED

RESTRICTED

49.

Orlando Number	Name	Repellent Time		M _D (22°)	b.p./mm.	Irrit. Exp.	
		Aedes	Anopheles			Index	Method
6538	Pyruvic acid, cyclohexyl ester	2(59-62)61	2(62-65)64	1.4509	56/0.3	1.3	31
6540	Pyruvic acid, 4-methylcyclohexyl ester	2 d	2 d	1.4483	63/0.25	2.7	31
6543	Pyruvic acid, 2-butoxyethyl ester	5(69-173)121	5(52-84)68	1.4265	82/0.25	0.3	31
6491	Pyruvic acid, 2-(2-ethoxyethoxy)ethyl	0 d	2(32-60)46	1.4409	90/0.25	7.3	31
6000	Acetoacetic acid, methyl ester	2(29)	2.21	1.4166	74/22.0		1
6493	Acetoacetic acid, amyl ester	2(47-56)52	2(30-30)30	1.4307	73/0.6	3.0	32
649C	Acetoacetic acid, hexyl ester	2(59-64)62	2(32-60)46	1.4322	80/0.25	5.0	32
6473	Acetoacetic acid, 2-ethylbutyl ester	2(49-84)67	2(51-54)53	1.4344	72/0.2	3.7	32
6479	Acetoacetic acid, heptyl ester	2(43-94)71	2(48-51)50	1.4347	82/0.1	3.3	32
6506	Acetoacetic acid, 2-ethylhexyl ester	6(28-60)42	6(30-62)44	1.4383	93/0.25	1.0	32
6489	Acetoacetic acid, cyclopentyl ester	3(19-22)61	3(22-44)22	1.4522	82/0.2	4.7	32
623C	Acetoacetic acid, cyclohexyl ester	41(15-275)101	39(15-226)47	1.4582	82/0.3	1.3	32
6432	Acetoacetic acid, 2-methylcyclohexyl ester	2(18-130)102	2(60-91)76	1.4566	87/0.2	1.0	32
6431	Acetoacetic acid, 3-methylcyclohexyl ester	2(14-22)53	2(18-25)22	1.4550	95/0.25	0.7	32

RESTRICTED

RESTRICTED

50.

Orlando Number	Name	Repellent Time		N _D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
		Acetes	Anopheles				
643C	Acetoacetic acid, 4-methyl- cyclohexyl ester	4(115-142)128	4(38-58)50	1.4572	95/0.2	3.3	32
6509	Acetoacetic acid, 2-ethoxy- ethyl ester	2(72-102)87	2(40-40)40	1.4312	81/0.25	0.3	32
6510	Acetoacetic acid, 2-butoxy- ethyl ester	2(76-136)106	2(46-47)47	1.4342	86/0.25	0.0	32
6508	Acetoacetic acid, 2-(2-ethoxy- ethoxy) ethyl ester	2(42-44)43	2(45-45)45	1.4405	100/0.25	0.7	32
6517	Acetoacetic acid, tetrahydro- furfuryl ester	4(72-156)109	4(30-78)46	1.4569	86/0.25	2.3	32
6229	Acetoacetic acid, benzyl ester	6(37-163)101	4(32-42)32	1.5098	105/0.3	1.3	32
6231	Acetoacetic acid, phenethyl ester	6(85-129)152	4(30-43)37	1.5055	111/0.3		32
6367	Glycol, bis(acetoacetate)	2(97-114)106	2(15-32)24	1.4551	140-150/0.2	1.3	32
6006	Acetoacetic acid, α -ethyl- ethyl ester	2(30-31)31	2(28-31)30	1.4197	95/24.0		1
6005	Acetoacetic acid, α -propyl- ethyl ester	3(14-70)34	3(14-67)34	1.4247	111/24.0		1
6003	Acetoacetic acid, α -butyl- ethyl ester	5(9-99)61	5(11-100)52	1.4259	130/37.0		1
6004	Acetoacetic acid, α -amyl- ethyl ester	2(13-14)14	2(11-12)12	1.4287	135/24.0		1
6228	Levulinic acid, cyclohexyl ester	4(133-265)177 2(242/286)	2(39-52)46 2(46/60)	1.4559	91/0.3		13

RESTRICTED

51.

RESTRICTED

Orlando Number	Name	Repellent Time		N _D (22°)	b.p. °/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6472	Cyclopentanecarboxylic acid, 2-oxo-, cyclopentyl ester	17(84-456)250	15(33-152)57	1.4739	102/1.0	4.3	32
6429	Cyclopentanecarboxylic acid, 2-oxo-, cyclohexyl ester	2(54-54)54	2(20-20)20	1.4762	114/2.0	2.3	32
6433	Cyclopentanecarboxylic acid, 2-oxo-, 2-ethoxyethyl ester	2(91-130)111	2(14-21)18	1.4543	102/0.5	1.0	32
6473	Cyclopentanecarboxylic acid, 2-oxo-, 2-butoxyethyl ester	4(81-276)137	4(40-105)63	1.4550	110/0.3	4.7	32
6471	Cyclopentanecarboxylic acid, 2-oxo-, tetrahydrofurfuryl ester	4(77-96)54	4(33-56)18	1.4779	117/1.0	2.0	32
6535	2-Cyclohexene-1-carboxylic acid, 2,6-dimethyl-4-oxo-, ethyl ester	14(47-393)181	4(35-73)55	1.4799	96/0.3	0.0	33
6534	2-Cyclohexene-1-carboxylic acid, 6-ethyl-2-methyl-4-oxo-, ethyl ester	12(66-427)208	12(23-61)41	1.4814	105/0.5	0.7	33
6533	2-Cyclohexene-1-carboxylic acid, 6-isopropyl-2-methyl-4-oxo-, ethyl ester	2(45-45)45	2(47-48)48	1.4811	103/0.5	0.7	33
6515	2-Cyclohexene-1-carboxylic acid, 2-methyl-4-oxo-6-propyl-, ethyl ester	4(23-94)68	4(19-30)26	1.4796	112/1.0	5.0	33
6163	Succinic acid, α,β -diacetyl-, diethyl ester	3 d	0 d				34
6002	Glutaric acid, β -oxo-, diethyl ester	8(96-323)167	8(29-52)32	1.4378	125/6.0		1

RESTRICTED

RESTRICTED

55.

Orlando Number	Name	Repellent Time Aedes	Anopheles	n_D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
6153	Pimelic acid, γ -oxo-, diethyl ester	2(40-76)58	6(17-37)28	1.4392	147/2.0		35
6560	2-Cyclohexene-1,5-dicarboxylic acid, 2,6-dimethyl-4-oxo-, diethyl ester	4(38-123)88	4(25-41)32	1.4314	125/0.3	1.3	33
Hydroxy-Esters							
6194	Butyric acid, β -hydroxy-, α -propyl-, ethyl ester	2(65-66)66	2(65-68)67	1.4297	125/29	1.3	37
6189	Butyric acid, α -amyl-, β -hydroxy-, ethyl ester	2(40-119)80	2(22-42)32	1.4345	75/1	1.7	37
6174	Valeric acid, α -hydroxy-, cyclohexyl ester	2(85-122)104		1.4557	78/0.5	5.0	13, 9
6146	Caprylic acid, α -hydroxy-, propyl ester	4(124-170)144	7(16-30)61	1.4318	87/0.5		13, 9
6148	Caprylic acid, α -hydroxy-, isopropyl ester	4(139-185)167	6(33-101)61	1.4277	77/0.5		13, 9
6145	Caprylic acid, α -hydroxy-, butyl ester	8(137-300)209	10(30-175)92	1.4345	96/0.5		13, 9
6149	Caprylic acid, α -hydroxy-, isoamyl ester	6(18-186)101	8(30-100)61	1.4356	104/0.5		13, 9
6141	Cyclopentanecarboxylic acid, 1-hydroxy-, propyl ester	4(31-182)90	6(11-80)36	1.4481	74/2		13, 9
6140	Cyclopentanecarboxylic acid, 1-hydroxy-, isoamyl ester	4(115-176)142	6(25-35)97	1.4495	78/0.5		13, 9

RESTRICTED

53.

RESTRICTED

Orlando Number	Name	Repellent Time		ND (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
		Aedes	anopheles				
6139	Cyclopentanecarboxylic acid, 1-hydroxy-, cyclopentyl ester	6(195-282)237	6(44-83)66	1.4710	85/0.5		13, 9
6138	Cyclopentanecarboxylic acid, 1-hydroxy-, cyclohexyl ester	10(47-385)236	10(27-71)47	1.4745	97/0.5		13, 9
6500	Cyclopentanecarboxylic acid, 1-hydroxy-, 2-butoxyethyl ester	8(142-438)267	8(24-61)38	1.4526	98/0.5	2.0	13, 9
6450	Cyclopentanecarboxylic acid, 1-hydroxy-, tetrahydrofurfuryl ester	4(26-252)117	4(26-42)41	1.4753	108/0.8	2.3	9, 13
6137	Cyclohexanecarboxylic acid, 1-hydroxy-, propyl ester	4(29-95)74	6(30-50)41	1.4536	72/0.5		9, 13
6136	Cyclohexanecarboxylic acid, 1-hydroxy-, isamyl ester	6(130-255)194	6(22-64)35	1.4543	89/0.5		9, 13
6209	Cyclohexanecarboxylic acid, 1-hydroxy-, 2-ethylbutyl ester	2(58-153)106		1.4572	92/0.5		9, 13
6133	Cyclohexanecarboxylic acid, 1-hydroxy-, cyclopentyl ester	24(14-523)236	26(8-76)33	1.4751	99/0.8		9, 13
6134	Cyclohexanecarboxylic acid, 1-hydroxy-, cyclohexyl ester	7(84-444)258	7(20-268)78	1.4772	107/0.5		9, 13
6497	Cyclohexanecarboxylic acid, 1-hydroxy-, 2-methoxyethyl ester	4(143-162)153	4(54-93)76	1.4615	86/0.5	0.7	9, 13
6494	Cyclohexanecarboxylic acid, 1-hydroxy-, 2-ethoxyethyl ester	10(73-308)227	8(51-56)42	1.4581	84/0.25	2.3	9, 13

RESTRICTED

RESTRICTED

54.

Orlando Number	Name	Repellent Time		N _D (22°)	b.p. °/mm.	Irrit. Index	Exp. method
		Aedes	Anopheles				
6493	Cyclohexanecarboxylic acid, 1-hydroxy-, 2-butoxyethyl ester	10(35-455)211	3(92-117)63	1.4565	113/0.5	0.3	9, 13
6413	Cyclohexanecarboxylic acid, 1-hydroxy-, tetrahydrofurfuryl ester	2(77-104)91	2(16-19)13	1.4802	107/0.5	2.7	9, 13
6608	Cyclohexanecarboxylic acid, 1-hydroxy-, acetyl ester	10(169-368)256	6(36-58)46	1.4734	92/0.1	2.0	30
6611	Mixture: R612 (50%) + Acetyl 1-hydroxycyclohexane- carboxylate	4(254-353)305	4(41-71)56			1.3	
6203	Cyclohexanecarboxylic acid, 1-hydroxy-, 2-hydroxyethyl ester	2(17-13)13		m.p. 79°		4.3	36
6202	Cyclohexanecarboxylic acid, 1-hydroxy-, 3-hydroxypropyl ester	2(41-69)55			127/0.5		36
6596	Cyclopentanecarboxylic acid, 1- hydroxy-, cyclohexyl ester	6(182-410)320	4(36-71)54	1.4750	112/0.2	5.3	38
6201	Cyclohexanecarboxylic acid, 1-hydroxy-, ethyl ester	7(136-402)244	5(19-116)44	1.4647	86/2		38
6225	Cyclohexanecarboxylic acid, 1- hydroxy-, propyl ester	10(123-375)238	8(28-75)41	1.4613	102/3	1.3	38
6226	Cyclohexanecarboxylic acid, 1- hydroxy-, butyl ester	22(85-404)255	20(31-75)46	1.4620	107/1	2.3	38

RESTRICTED

RESTRICTED

55.

RESTRICTED

Orlando number	Name	Repellent Time		N _D (22°)	b.p.°/mm.	Irrit. Index	Exp. method
		Aedes	Anopheles				
6599	Cyclohexanecarboxylic acid, 1-hydroxy-, isoamyl ester	10(167-305) <u>212</u>	6(34-51) <u>41</u>	1.4608	110/1	2.0	38
6600	Cyclohexanecarboxylic acid, 1-hydroxy-, cyclopentyl ester	10(202-392) <u>271</u>	6(50-53) <u>40</u>	1.4842	117/0.8	2.7	38
6606	dl-Malic acid, acetonide ester	4(50-280) <u>116</u>	4(40-56) <u>48</u>	1.5239	134/0.2	2.3	30
6220	Hydroacrylic acid, 3-phenyl-, methyl ester	16(75-459) <u>222</u>	14(20-74) <u>36</u>	1.5188	122/1		38
6216	Hydroacrylic acid, 3-phenyl-, ethyl ester	33(33-497) <u>268</u>	31(16-73) <u>32</u>	1.5082	124/1		38
6217	Hydroacrylic acid, 3-phenyl-, isopropyl ester	20(212-541) <u>344</u>	18(11-68) <u>37</u>	1.4992	125/1	2.0	38
6218	Hydroacrylic acid, 3-phenyl-, propyl ester	12(99-529) <u>284</u>	10(24-76) <u>36</u>	1.5036	129/1		38
6219	Hydroacrylic acid, 3-phenyl-, butyl ester	8(50-362) <u>154</u> 4(210/227)	6(26-67) <u>38</u> 4(34/43)	1.4992	133/1		38
6223	Butyric acid, 3-hydroxy-, 3-phenyl-, methyl ester	4(124-173) <u>138</u>	2(31-57) <u>44</u>	1.5039	117/1		38
6221	Butyric acid, 3-hydroxy-, 3-phenyl-, ethyl ester	9(30-330) <u>209</u>	6(15-72) <u>36</u>	1.5001	122/1		38
6224	Butyric acid, 3-hydroxy-, 3-phenyl-, isopropyl ester	8(137-417) <u>352</u>	6(28-84) <u>47</u>	1.4908	128/3		38
6222	Butyric acid, 3-hydroxy-, 3-phenyl-, propyl ester	2(99-118) <u>109</u>		1.4957	126/1		38

56.

RESTRICTED

Orlando Number	Name	Repellent Time		N _D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6116	Glycol, monoisobutyrate	2(34-77)56	2(37-33)38	1.4211	116/44		36
6103	Glycol, monocaproate	11(123-305)200	11(24-150)60	1.4322	110/5		36
6115	Glycol, monomethanate	3(22-154)113	3(24-31)27	1.4359	98/0.5		36
6534	Glycol, monobenzate	6(41-122)79	6(22-27)24	1.5325	120/2	3.0	7
6364	Glycol, monomethanate	2(64-65)65	2(29-30)30	1.5322	143/0.4	1.0	7
6526	1,2-Ethanediol, 1-phenyl-2-propionate	10(95-446)237	10(30-63)43	1.5124	99/0.2	2.5	39
6359	1,2-Propanediol, 1-(2-ethylbutyrate)	2(59-96)78	2(28-30)29	1.4267	62/0.2	1.3	36
6333	1,2-Propanediol, 1-caproate	8(77-284)209	8(16-205)30	1.4313	77/0.3	1.0	40
6628	1,2-Propanediol, monomethanate	4(23-204)113	4(26-40)34	1.4339	95/0.3	4.3	36
6523	1,2-Propanediol, 1-benzoate	2(35-76)56	2(37-38)38	1.5197	105/0.25	3.5	36
6529	1,2-Propanediol, 1- <i>o</i> -toluate	4(29-146)35	4(21-39)29	1.5080	113/0.3	3.0	36
6114	1,3-Propanediol, monoisobutyrate	2(62-62)62	2(63-66)65	1.4239	92/2.5		36
6094	1,3-Propanediol, monocaproate	6(17-302)207	6(18-57)37	1.4347	125/5		36
6373	1,3-Propanediol, monobenzoate	7(131-474)302	8(30-68)44	1.5250	145/3	3.0	7
6311	1,3-Propanediol, mono(phenylacetate)	0.4	0.4	m.p. 89°		0	7
6627	1,4-Butanediol, monovalerate	4(108-137)154	4(41-50)45	1.4355	95/0.3	2.0	36
6317	1,5-Pentanediol, monopropionate	8(119-336)217	10(26-123)50	1.4340	100/0.8	1.3	7

RESTRICTED

RESTRICTED

57.

Orlando Number	Name	Repellent Time		N _D (22°)	b.p. °mm.	Irrit. Index	Exp. method
		Aedes	Anopheles				
6614	1,5-Pentanediol, monobutyrate	2(115-163)139	2(30-30)30	1.4360	97/0.4	2.7	7
6351	1,5-Pentanediol, monoacproate	2(50-105)78	2(25-27)26	1.4410	114/0.1	3.0	40
6387	1,5-Pentanediol, monomanthate	9(119-421)262	3(14-45)35	1.4431	119/2	3.3	7
6437	1,2-Cyclohexanediol, mono- acetate	2(23-35)54	2(21-26)24	1.4591	94/0.5	1.3	7
6613	1,2-Cyclohexanediol, trans- monoacetate	2(46-139)23	2(25-49)37	1.4628	127/18	4.0	60
6616	1,2-Cyclohexanediol, mono- propionate	3(128-154)145	3(31-35)32	1.4634	89/0.4	1.7	41
6254	1,3-Cyclohexanediol, mono- propionate	31(17-448)250	31(18-201)52	1.4563	88/0.2	4.3	42
5257	1,3-Cyclohexanediol, mono- butyrate	8(166-412)267	8(12-61)45	1.4586	98/0.2	2.0	7
6602	1,4-Cyclohexanediol, mono- propionate	10(228-387)311	6(32-59)47	1.4623	91/0.5	2.0	43
6406	Resorcinol, monopropionate	2(18-21)20	2(17-17)17	1.5201	119/0.2	0.3	20
6533	dl-Malic acid, diallyl ester	2(24-56)40	2(26-33)30	1.4624	96/0.3	3.3	13
6575	dl-Malic acid, diisopropyl ester	2(114-120)117	2(33-66)47	1.4293	74/0.2	4.7	13
6532	dl-Malic acid, dipropyl ester	2(36-56)46	2(31-39)35	1.4364	87/0.2	2.7	13
5592	dl-Malic acid, di-sec-butyl ester	2(46-77)62	2(24-24)24	1.4345	91/0.25	5.7	13

RESTRICTED

RESTRICTED

Crlando Numb-r	Name	Repellent Time		N _D (22°)	b.p. °/mm.	Irrit. Index	Exp. method
		Aedes	Anopheles				
6262	1,3-Propanediol, dilactate	2(28-82)55	2(31-85)58	1.4545	140/0.001	2.0	13
6499	Isobutyric acid, β -acetoxy- α -hydroxy-, isoamyl ester	8(126-369)283	8(39-83)62	1.4329	89/0.5	1.0	44
6551	Isobutyric acid, β -acetoxy- α -hydroxy-, cyclohexyl ester	7(151-461)222	7(34-63)48	1.4545	109/0.5	1.3	44
6466	1,3-Dioxolane-2-propionic acid, 4-hydroxymethyl-2-methyl-, ethyl ester	4(51-169)122	4(57-82)72	1.4515	101/0.3	1.7	28
Ethers							
6271	Cyclohexanone, dibutyl ketal	2(19-20)20	2(22-23)23	1.4476	95/18	6.3	28
6442	Cinnamaldehyde, diethyl acetal	2(48-48)48	2(21-22)22	1.5139	96/0.25	1.3	50
6453	1(2)-Naphthalenone, octahydro-, diethyl ketal	7 d	0 d	1.4867	79/0.2	4.7	50
6452	1,3-Benzodioxole, 2,2-penta- methylene	0 d	0 d	m.p. 49°	67/0.1	2.0	28
6612	1,4-Dioxaspiro(4.5)decane, 8- methyl-2,3-tetramethylene-	2(42-53)48	2(22-44)33	1.4793	82/0.4		49
6519	Orthoformic acid, triamyl ester	2(41-41)41	2(43-44)44	1.4194	153/8	5.3	1
6447	Orthoformic acid, bornyl diethyl ester	2(13-20)17	2(15-23)19	1.4517	89/0.5	3.0	45
6446	Orthoformic acid, tris(2- methoxyethyl)	2(16-45)31	2(17-19)18	1.4257	265/760	2.7	46

RESTRICTED

RESTRICTED

Grando Number	Name	Repellent Time		n _D (22°)	b.p. °/mm.	Irrit. Exp.	
		Aedes	Anopheles			Index	Method
6537	Orthocarbonic acid, tetra(2-methoxyethyl) ester	2(34-136)85	2(24-37)31	1.4305	158/7	4.0	81
6536	Orthoacetic acid, triamyl ester	2(47-47)47	2(50-51)51	1.4266	124/5	1.0	46
6623	Orthopropionic acid, triisomyl ester	2(9-53)31	2(12-23)18	1.4264	120/4	3.7	46
6622	Orthobenzoic acid, tripropyl ester	0 d	0 d	1.4714	119/1.5	7.7	47
6431	Propionaldehyde, β -ethoxy-, diethyl acetal	2(13-44)24	4(17-25)20	1.4875	82/21	5.0	48
6432	Propionaldehyde, β -ethoxy-, dipropyl acetal	2(25-41)33	2(28-44)26	1.4157	67/0.3	4.0	49
6433	Propionaldehyde, β -ethoxy-, dibutyl acetal	2(26-56)42	4(27-36)20	1.4237	101/0.2	5.7	49
6443	Anisaldehyde, diethyl acetal	2(16-72)44	2(45-46)46	1.5030	85/0.2	1.3	50
6459	1,3-Dioxolane, 2-(2-(2-furyl)-vinyl)-2-methyl-	7 d	0 d	1.5417	64/0.15	4.7	28
6436	1,3-Benzodioxole, 2-(2-ethoxyethyl)-hexahydro-	2(96-91)64	2(34-37)36	1.4581	78/0.3	1.7	49
6444	1,3-Benzodioxole, hexahydro-2-(p-methoxyphenyl)-	2(43-79)61	2(45-51)48	1.5357	141/0.4	1.7	49
6527	1,3-Dioxolane, 2-(2-furyl)-4-methoxymethyl-	2(73-104)82	2(27-33)20	1.4775	75/0.2	5.0	28
6162	3-Butene-2-one, 4-(2-furyl)-	2(18) 20 + d		m.p. 37°	116/10	1	53
6463	1,3-Dioxolane, 2-(o-hydroxyphenyl)-	2 d	0 d	m.p. 58°		1.3	28

RESTRICTED

RESTRICTED

Orlando Number	Name	Repellent Time Aedes	Anopheles	n_D (20°)	b.p. °/mm.	Irrit. Index	Exp. Method
6501	Ethanol, 2-ethoxy-1-phenyl-	10(60-262)167	3(28-50)42	1.5094	63/0.25	0.7	51
6503	Ethanol, 1-phenyl-2-propoxy-	14(180-387)262	12(36-96)60	1.5037	75/0.2	1.3	51
6504	Ethanol, 2-isobutoxy-1-phenyl-	4(29-135)100	4(25-53)40	1.4960	81/0.2	1.3	51
6505	Ethanol, 2-(2-methoxyethoxy)-1-phenyl-	2(57-112)85	2(60-82)71	1.5098	99/0.2	2.3	51
6227	2-Butanol, 4-(2-furyl)-	4(64-76)70	2(17-17)17	1.4669	112/35		52
6206	2-Butanol, 4-(2-tetrahydrofuryl)-	4(94-102)92	2(27-28)28	1.4539	79/0.5		52
6476	1,3-Dioxolane-4-methanol, 2-(2-furyl)- and 5-m-dioxanol, 2-(2-furyl)-	4(107-149)127	4(30-63)42	1.5022	100/0.3	5.0	28
Ketones							
6136	1(2)-Naphthaleneone, octahydro-	7(13-168)83	7(30-62)44	1.4846		2.7	1
6210	6-Dodecanone, 7-hydroxy	12(52-127)234	10(27-206)93	1.4398	85/0.5		54
Alcohols							
6259	$\Delta^{10,11}$ -Undecylenol-1	0 d	0 d	1.4488	118/30M	7.3	1
6131	Benzyl alcohol, α -hexyl-	3(15-60)41	2(10-62)30		157/15.0		1
6130	Benzyl alcohol, α , α -dimethyl	4(56-62)52	2(60-101)80		83/5.0		1
6119	Benzyl alcohol, α -isopropyl- α -methyl-	2(75-123)92	2(29-29)22	1.5190	117/20		1
6204	α -Naphthol, decahydro-	4(61-132)104	2(34-34)34	1.4948	77/0.5	6.0	55

RESTRICTED

RESTRICTED

61.

RESTRICTED

Orlando Number	Name	Repellent Time Aedes.	Anopheles	N _D (22)	b.p. °/mm.	Irrit. Index	Exp. Method
6225	1,9-Nonenediol	2(23-39)31	2(26-42)34	m.p. 45°	160/7.0	1.7	56
6165	3,4-Hexanediol, 3,4-diethyl-	3(130-215)169	5(90-102)96		117/17.0		57
6458	1,2-Cyclohexanediol, <u>trans</u> -	O d	O d	m.p. 102°			55
6457	1,2-Cyclohexanediol, <u>cis</u> and <u>trans</u> 1 d		O d	m.p. 76°			55
6234	1,3-Cyclohexanediol, <u>cis</u> and <u>trans</u> -	2(54-54)54			110/6.3		55
6233	1,3-Cyclohexanediol, 4-hexyl-, 2(25-28)27			1.4778			55
6464	1,4-Cyclohexanediol, <u>cis</u> -	O d	O d	m.p. 99°		1.0	55
Amides							
6147	Butyramide, N,N-diethyl	4(62-146)104	6(45-62)53	1.4373	109/25		58
6469	Phthalimide, N-isopropyl-	O d	O d	m.p. 79°	93/1	1.0	59
6470	Phthalimide, N-allyl-	O d	O d	m.p. 70°	97/1	1.7	59
6465	Phthalimide, N-propyl-	10 + d	O d	m.p. 65°	98/1	5.0	59
6198	Succinimide, N-(1-dioethylamino-4-aryl)-	O d	O d	1.4788	116/0.5	8.0	59
6183	Carbamic acid, N,N-dibutyl-, ethyl ester	2(55-59)57	2(19-20)20	1.4309	113/20	5.3	67
6182	Carbamic acid, N,N-diamyl-, ethyl ester	2(35-48)42	2(15-32)24	1.4361	85/0.5	6.0	67
6409	Carbamic acid, N,N-dioctyl-, hexyl-, methyl ester	O d	O d	m.p. 57°	119/1	3.0	67

62.

RESTRICTED

Orlando Number	Name	Repellent Time Aedes	Anopheles	N_D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
6327	Carbamic acid, N,N-dicyclohexyl- ethyl ester	6(26-60) <u>45</u>	6(21-51) <u>24</u>	1.4838	122/1	1.0	67
6181	Carbamic acid, N-methyl-N- phenyl-, ethyl ester	2(71-123) <u>27</u>	2(31-85) <u>58</u>	1.5142	81/0.5	4.3	67
6187	Carbamic acid, N-ethyl-N- phenyl-, ethyl ester	2(55-105) <u>80</u>	2(56-106) <u>81</u>	1.5052	75/0.5	4.0	67
6416	Carbamic acid, N-methyl-N- phenyl-, butyl ester	2(20-46) <u>33</u>	2(19-23) <u>21</u>	1.5042	107/1	2.3	67
6419	Carbamic acid, N-ethyl-N- phenyl-, butyl ester	2(21-21) <u>21</u>	2(24-24) <u>24</u>	1.4992	108/1	2.9	67
6410	Carbamic acid, N-butyl-N-phenyl-, methyl ester	0 d	0 d	1.5087	103/1	8.0	67
6411	Carbamic acid, N-butyl-N- phenyl-, ethyl ester	2(22-51) <u>37</u>	2(25-54) <u>40</u>	1.5003	107/1	1.0	67
6412	Carbamic acid, N-butyl-N- phenyl-, butyl ester	2(20-22) <u>21</u>	2(23-23) <u>23</u>	1.4920	115/1	1.2	67
6207	Carbamic acid, N,N-dicarboxy-, triethyl ester	9(25-318) <u>194</u>	7(27-188) <u>71</u>		146/12		1
6185	Carbamic acid, N-(1-diethyl- amino-4-ethyl)-, ethyl ester	10 + d	0 d	1.4520	93/0.5	7.3	67
6184	4-Morpholinecarboxylic acid, ethyl ester	2(56-56) <u>56</u>	2(20-59) <u>40</u>	1.4574	105/15	3.0	67
6267	Succinamic acid, N-butyl-, ethyl ester	2(51-89) <u>70</u>	2(20-29) <u>25</u>	1.4537	134/1	2.3	61.

RESTRICTED

63.

RESTRICTED

Orlando Number	Name	Repellent Time		N _D (22°)	b.p.°/mm.	Irrit. Index	Exp. method
		Aedes	Anopheles				
6340	Succinamic acid, N-butyl-, propyl ester	2(93-157)125	2(30-32)31	1.4525	130/0.3	2.7	61
6621	Succinamic acid, N,N-dimethyl-, propyl ester	2(76-96)86	2(10-20)15	1.4527	91/0.1	2.3	61
6166	Succinamic acid, N,N-diethyl-, ethyl ester	10(142-407)247	12(23-166)46	1.4507	106/1	0.7	61
6617	Succinamic acid, N,N-diethyl-, allyl ester	2(17-54)25	2(19-21)20	1.4640	101/0.4	2.7	61
6168	Succinamic acid, N,N-diethyl-, propyl ester	45(16-474)322	47(8-162)76	1.4515	107/0.5	2.4	61
6172	Succinamic acid, N,N-diethyl-, isopropyl ester	9(168-384)255	10(13-33)72	1.4479	99/0.5		61
6388	Succinamic acid, N,N-diethyl-, sec-butyl ester	9(238-456)377	8(6-96)46	1.4495	106/0.5	3.0	61
6275	Succinamic acid, N,N-diethyl-, isobutyl ester	2(24-28)26	2(31-56)44	1.4497	114/1	5.0	61
6241	Succinamic acid, N,N-diethyl-, butyl ester	2(27-54)41	2(29-30)30	1.4475	119/1	4.7	61
6398	Succinamic acid, N,N-diethyl-, 2-methoxyethyl ester	2(29-55)42	2(31-31)31	1.4573	121/0.3	0.3	61
6332	Succinamic acid, N,N-tetra- methyleno-, propyl ester	2(47-109)78	2(29-30)30	1.4720	125/0.5	2.3	62
6403	Succinamic acid, N,N-penta- methyleno-, methyl ester	2(20-53)37	2(22-22)22	1.4826	123/1	1.7	61

RESTRICTED

RESTRICTED

RESTRICTED

Orlando Number	Name	Repellent Time Aedes	n_D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
6404	Succinamic acid, N,N-penta- methylene-, ethyl ester	2(25-49)27	1.4765	144/2	2.3	62
6328	Succinamic acid, N,N-penta- methylene-, isopropyl ester	12(31-247)193	1.4728	115/0.4	0.0	61
6246	Succinamic acid, N,N-penta- methylene-, propyl ester	8(71-450)247	1.4754	126/0.5	2.7	62
6230	Succinamic acid, N,N-penta- methylene-, isobutyl ester	2(14-15)15	1.4726	141/1	3.0	61
6396	Succinamic acid, N,N-diisopropyl-, methyl ester	2(65-67)66	1.4523	108/1	1.3	62
6405	Succinamic acid, N,N-diisopropyl-, ethyl ester	4(38-154)90	1.4504	109/1	1.3	61
6350	Succinamic acid, N,N-diisopropyl-, isopropyl ester	11(21-486)310	1.4475	98/0.5	1.0	62
6348	Succinamic acid, N,N-diisopropyl-, propyl ester	8(137-451)341	1.4513	105/0.5	1.0	62
6390	Succinamic acid, N,N-diisopropyl-, sec-butyl ester	12(96-466)257	1.4486	105/0.4	3.7	62
6399	Succinamic acid, N,N-diisopropyl-, 2-methoxyethyl ester	2(50-115)83	1.4549	117/0.25	1.3	62
6400	Succinamic acid, N,N-dipropyl-, methyl ester	2(19-101)60	1.4543	114/1	2.7	61
6252	Succinamic acid, N,N-dipropyl-, ethyl ester	4C(19-428)207	1.4521	120/1	2.3	62

65.

RESTRICTED

Orlando Number	Name	Repellent Time		n _D (22°)	b.p. °/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6619	Succinamic acid, N,N-dipropyl-, allyl ester	2(45-77)61	2(17-27)22	1.4631	117/0.2	3.0	62
6269	Succinamic acid, N,N-dipropyl-, isopropyl ester	2(60-62)61	2(25-27)26	1.4495	108/0.4	5.0	62
6251	Succinamic acid, N,N-dipropyl-, propyl ester	8(146-329)218 O d	8(23-59)37	1.4527	117/0.5	5.0	62
6393	Succinamic acid, N,N-dipropyl-, sec-butyl ester	8(108-477)318	8(33-50)41	1.4505	120/0.5	2.3	61
6402	Succinamic acid, N,N-diisobutyl-, methyl ester	4(47-331)180	8(18-65)38	1.4536	122/1	2.7	61
6408	Succinamic acid, N,N-diisobutyl-, ethyl ester	2(48-48)48	2(20-20)20	1.4516	124/1	1.7	61
6200	Succinamic acid, N,N-dibutyl-, ethyl ester	4(46-170)25	4(39-54)46		117/0.5	1	13
6245	Succinamic acid, N,N-dibutyl-, propyl ester	2(34-51)43	2(23-36)30	1.4532	134/0.5	2.7	62
6249	Succinamic acid, N,N-diethyl-, ethyl ester	2(32-49)46	2(36-36)36	1.4540	143/1	3.0	62
6248	Succinamic acid, N,N-diethyl-, propyl ester	2(22-36)22	2(24-40)32	1.4544	147/0.5	2.7	62
6178	4-Morpholinebutyric acid, oxo-, ethyl ester	O d	O d		126/0.5		13
6570	4-Morpholinebutyric acid, oxo-, isopropyl ester	2(19-69)44	2(22-62)52	1.4740	191/0.5	0.7	61

RESTRICTED

RESTRICTED

66.

Orlando Number	Name	Repellent Time		n _D (20°)	b.p. °/mm.	Irrit. Exp. Index Method
		Aedes	Anopheles			
6335	Maleamic (Fumaramio?) acid, N,N-diethyl-, ethyl ester	8(115-405)261	8(39-91)51	1.4707	115/1	2.0 63
6336	Maleamic (Fumaramio?) acid, N,N-pentamethylene-, ethyl ester	5(104-445)268	5(31-40)35	1.4981	137/1	1.0 63
6369	Glutaramio acid, N,N-diethyl-, methyl ester	8(68-428)300	8(32-69)48	1.4560	100/0.4	1.7 61
6361	Glutaramio acid, N,N-diethyl-, ethyl ester	6(57-184)138	6(11-44)32	1.4537	104/0.4	1.7 61
6395	Glutaramio acid, N,N-diethyl-, propyl ester	2(44-112)78	2(18-19)19	1.4523	106/0.3	1.0 61
6375	Glutaramio acid, N,N-diisopropyl-, methyl ester	10(95-407)248	10(16-65)32	1.4547	104/0.5	2.7 62
6358	Glutaramio acid, N,N-diisopropyl-, ethyl ester	15(26-519)232	16(20-49)37	1.4526	107/0.4	1.7 62
6397	Glutaramio acid, N,N-diisopropyl-, propyl ester	8(83-476)244	8(22-48)36	1.4517	109/0.3	2.3 62
6373	Glutaramio acid, N,N-dipropyl-, methyl ester	13(74-474)230	15(25-50)32	1.4561	114/0.5	0.7 62
6365	Glutaramio acid, N,N-dipropyl-, ethyl ester	10(41-477)264	10(13-67)32	1.4540	116/0.5	1.3 62

RESTRICTED

RESTRICTED

Orlando Number	Name	Repellent Time		n _D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6374	Glutaramic acid, N,N-penta- methylen-, methyl ester	2(99-159) <u>122</u>	2(34-34) <u>34</u>	1.4872	123/0.5	1.0	61
6362	Glutaramic acid, N,N-penta- methylen-, ethyl ester	2(57-79) <u>63</u>	2(17-17) <u>17</u>	1.4782	128/0.5	1.3	61
6620	Adipamic acid, N,N-dimethyl-, isopropyl ester	2(60-164) <u>112</u>	2(32-32) <u>32</u>	1.4527	106/0.1	2.0	61
6437	Adipamic acid, N,N-diethyl-, methyl ester	2(32-89) <u>61</u>	2(34-34) <u>34</u>	1.4563	111/1	1.3	61
6511	Adipamic acid, N,N-diethyl-, ethyl ester	3(254-353) <u>276</u>	4(41-71) <u>56</u>	1.4546	115/1	4.7	61
6613	Adipamic acid, N,N-diethyl-, isopropyl ester	2(56-133) <u>97</u>	2(23-24) <u>24</u>	1.4515	106/0.1		61
6434	Adipamic acid, N,N-diisopropyl-, methyl ester	14(101-503) <u>243</u>	10(30-78) <u>51</u>	1.4560	110/0.5	1.3	62
6436	Adipamic acid, N,N-diisopropyl-, ethyl ester	2(99-100) <u>100</u>	2(45-45) <u>45</u>	1.4586	126/0.5	1.7	62
6435	Adipamic acid, N,N-dipropyl-, methyl ester	2(28-93) <u>61</u>	2(31-39) <u>35</u>	1.4572	121/0.5	1.3	62
6273	Acetamide, N-ethyl-N-(2- acetoxyethyl)-	2(64-65) <u>65</u>	2(33-50) <u>42</u>	1.4514	100/1	2.3	17
6277	Acetamide, N-butyl-N-(2- acetoxyethyl)-	2(19-91) <u>55</u>	2(21-24) <u>23</u>	1.4512	110/1	3.3	17
6303	Propionamide, N-ethyl-N- (2-propionoxyethyl)-	6(14-288) <u>167</u>	6(17-67) <u>42</u>	1.4512	110/1	3.0	17

RESTRICTED

68.

RESTRICTED

Orlando Number	Name	Repellent Aedes	Time Anopheles	n_D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
6310	Propionamide, N-butyl-N-(2-propionyloxyethyl)-	10(45-333)210	10(13-55)38	1.4530	117/1	2.3	17
6312	Butyramide, N-(2-butyroxyethyl)-N-ethyl-	10(41-431)211	10(30-65)44	1.4515	125/3	1.0	17
6315	Butyramide, N-butyl-N(2-butyroxyethyl)-	2(39-109)74	2(33-41)37	1.4518	132/1	1.7	17
6455	Formanilide, N-(2-formoxyethyl) 2(40-76)58	2(42-49)46	2(42-49)46	1.5521	134/2	1.0	18
6392	Propionanilide, N-(2-propionyloxyethyl)-	2(39-34)62	2(42-42)42	1.5065	138/1	2.0	17
6445	Succinimide-N-carboxylic acid, butyl ester	2(45-45)45	2(17-18)18	1.4306	112/1	2.0	64
6454	Succinimide-N-acetic acid, butyl ester	2(37-60)44	2(30-30)30		141/2	2.3	64
6553	Glutaramic acid, N,N-diethyl- α -hydroxy-N-methyl-, δ -lactone	2(55-101)78	2(53-62)60	1.4687	97/0.4	1.5	65
6594	Glutaramic acid, α -hydroxy-N-methyl-N,N-dipropyl-, δ -lactone	2(78-105)22	2(21-51)37	1.4683	105/0.2	3.3	65
6347	2-Pyrrolinc-3-carboxylic acid, 1-isopropyl-2-methyl-5-oxo-, ethyl ester	2(89-130)110	2(26-52)39	1.4875	126/3	2.7	66
6371	2-Pyrrolinc-3-carboxylic acid, 2-methyl-5-oxo-1-propyl-, ethyl ester	2(55-143)84	2(28-28)28	m.p. < 37°	130/2	2.7	66

RESTRICTED

69.

RESTRICTED

Orlando Number	Name	Repellent Time Aedes	ND (22°)	b.p. °/mm.	Irrit. Index	Exp. Method
6363	2-Pyrroline-3-carboxylic acid, 1-sec-butyl-2-methyl-5-oxo- ethyl ester	6(43-138)95	1.4891	130/2	1.7	66
6345	2-Pyrroline-3-carboxylic acid, 1-isobutyl-2-methyl-5-oxo- ethyl ester	0 d	<36	135/2	2.0	66
6342	2-Pyrroline-3-carboxylic acid, 1-butyl-2-methyl-5-oxo- ethyl ester	0 d	m.p. 75°	132/1	1.0	66
6376	2-Pyrroline-3-carboxylic acid, 1-amyl-2-methyl-5-oxo- ethyl ester	2(44-73)52	m.p. <37°	140/1	2.3	66
6389	Nicotinic acid, 1-butyl-1,4,5,6- tetrahydro-2-methyl-6-oxo- methyl ester	2(22-61)42		135/1	2.7	66
6386	Nicotinic acid, 1-amyl-1,4,5,6- tetrahydro-2-methyl-2-oxo- methyl ester	2(43-49)46	1.4980	135/1	2.0	60
6603	Acetamide, 1-butoxymethyl- diethyl	10 + d	1.4448	85/0.8	5.0	68
6605	Acetamide, 1-cyclohexoxymethyl- diethyl	10(203-390)291	1.4715	99/0.4	3.0	68
6532	1,3-Dioxolane-2-propionamide, N,N-diethyl-2-methyl-	2(39-88)60	1.4633	105/1	0.3	28
6512	1,3-Dioxolane-2-propionamide, 2-methyl-N,N-dipropyl	2(83-102)93	1.4609	112/1	6.7	28

RESTRICTED

RESTRICTED

70.

RESTRICTED

71.

Orlando Number	Name	Repellent Time		N _D (22°)	b.p. °/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6569	Acetoacetamide, N,N-diethyl-	2(76-111)24	2(49-82)66	1.4666	73/0.25	3.7	69
6558	Acetoacetamide, N,N-dipropyl-	2(22-92)57	2(25-57)41	1.4698	88/0.25	2.0	69
6565	Acetoacetamide, N,N-diisobutyl-	2(25-136)81	2(30-48)32	1.4680	95/0.25	0.3	69
6555	Acetoacetamide, N,N-dibutyl-	4(48-163)117	4(23-72)55	1.4679	106/0.3	3.7	69
6567	Acetoacetamide, N,N-penta- methylene-	2(54-69)62	2(26-43)35	1.4954	102/0.25	3.7	69
6568	Morpholine, 4-acetoacetyl-	2(46-79)63	2(23-49)36	1.4973	117/0.25	2.7	69
6513	Levulinamide, N,N-diethyl-	2(96-153)125	2(22-22)22	1.4574	90/1	6.3	70
6514	Levulinamide, N,N-diisopropyl-	6(141-414)220	6(17-68)42	1.4576	93/1	5.3	70
6461	Levulinamide, N,N-dipropyl-	9(40-366)205	9(30-61)40	1.4575	110/2	0.7	70
6531	Valeramide, 4-hydroxy-N,N- dipropyl-	2(42-44)43	2(45-45)45	1.4624	119/1	0.7	71
6601	Valeramide, 3-hydroxy-3-methyl- N,N-dipropyl-	10(308-360)296	6(27-60)43	1.4548	106/0.5	1.7	72
6563	Caproamide, N,N-diethyl-3- hydroxy-3-methyl-	10 + d	0 d	1.4556	94/0.3	8.0	72
6456	Cyclohexanecetamide, N,N- diethyl-1-hydroxy-	2(58-113)86	2(27-28)28	1.4601	100/0.3	1.7	72
6604	Cyclohexanecetamide, 1-hydroxy- N,N-diisopropyl-	10(171-392)277	6(29-56)32	1.4782	102/0.2	3.3	72
6561	Hydracrylamide, N,N-diethyl- 2-phenyl-	2(70-139)105	2(46-50)48	1.5248	139/0.3	2.3	72

RESTRICTED

RESTRICTED

Orlando Number	Name	Repellent Time Aedes	Repellent Time Anopheles	n_D (22°)	b.p. °/mm.	Irrit. Index	Exp. Method
6203	Hydrazinecarboxylic acid, ethyl ester	2 (102-103) <u>103</u>			93/13		1
Amines							
6518	Glycine, N-cyclohexyl-, ethyl ester	4 d		1.4570	85/0.2	8.0	74
6524	Glycine, N-benzyl-, ethyl ester 2 (97-147) <u>122</u>		2 (22-29) <u>26</u>	1.5050	105/0.3	2.7	74
6525	Glycine, N-benzyl-, butyl ester 8 (134-389) <u>252</u>		2 (28-74) <u>48</u>	1.4968	119/0.3	2.3	74
6516	Glycine, N,N-diethyl-, ethyl ester	2 (62-99) <u>89</u>	2 (24-43) <u>24</u>	1.4344	91/0.25	5.3	73
6539	Glycine, N,N-pentamethylene-, butyl ester	2 (63-90) <u>77</u>	3 (60-66) <u>62</u>	1.4526	80/0.25	3.3	73
6544	Glycine, N,N-pentamethylene-, cyclohexyl ester	8 (79-423) <u>256</u>	7 (31-65) <u>50</u>	1.4779	101/0.25	1.7	73
6545	4-Morpholinacetic acid, butyl ester	8 (20-266) <u>202</u>	7 (34-85) <u>55</u>	1.4527	90/0.2	1.2	73
6537	Glycine, N-methyl-N-phenyl-, ethyl ester	4 (40-195) <u>102</u>	2 (25-59) <u>47</u>	1.5294	97/0.3	0.0	73
6542	Glycine, N-ethyl-N-phenyl-, ethyl ester	5 (93-270) <u>154</u>	5 (23-53) <u>31</u>	1.5252	103/0.25	1.7	73
6559	Glycine, N-butyl-N-(2-hydroxy- ethyl)-, lactone	2 (73-102) <u>88</u>	2 (50-83) <u>67</u>	1.4601	89/0.4	4.0	75
6566	Glycine, N-(2-hydroxyethyl)- N-phenyl-, lactone	0 d	0 d	m.p. 67°	140/0.2	2.0	75

72.

RESTRICTED

Orlando Number	Name	Repellent Time		N _D (22°)	b.p. °/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6578	1-Pyrroleacetic acid, propyl ester	2(57-84) <u>71</u>	2(28-28) <u>28</u>	1.4766	67/0.4	5.0	76
6577	1-Pyrroleacetic acid, butyl ester	4(110-164) <u>132</u>	4(22-45) <u>36</u>	1.4753	75/0.4	4.0	76
6576	1-Pyrroleacetic acid, iso-amyl ester	2(26-82) <u>54</u>	2(29-30) <u>30</u>	1.4594	65/0.1	5.3	76
6581	1-Pyrroleacetic acid, cyclopentyl ester	8(58-319) <u>212</u>	8(32-54) <u>44</u>	1.4951	89/0.2	3.0	76
6580	1-Pyrroleacetic acid, cyclohexyl ester	0 d	0 d	m.p. 47°	105/0.5	7.3	76
6475	1,3-Dioxolane, 2-(p-diethylamino-phenyl)-	0 d	0 d	1.5776	105/0.2	7.7	28
6495	1,3-Dioxolane, 2-(p-dimethylaminophenyl)-4-methyl-	2(42-101) <u>72</u>	2(45-46) <u>46</u>	1.5615	105/0.2	3.0	28
6488	1,3-Dioxolane, 2-(p-diethylaminophenyl)-4-methyl-	2(29-35) <u>32</u>	2(32-38) <u>35</u>	1.5483	111/0.2	0.7	28
6572	Benzyl alcohol, -butyl-aminomethyl-	0 d	0 d	m.p. 55°	101/0.1	2.3	77
6573	Benzyl alcohol, -diethylaminomethyl-	9 d	0 d	1.5054	81/0.1	8.0	77
6591	Succinonitrile	0 d	0 d	m.p. 48°	266/760	2.0	1
6554	2-Propanone, 1-hydroxy-, acetate-, oxime	2(104-133) <u>112</u>	2(21-21) <u>21</u>	1.4562	78/0.5	1.0	78

Halogen

Orlando Number	Name	Repellent Time		N _D (22°)	b.p.°/mm.	Irrit. Index	Exp. Method
		Aedes	Anopheles				
6588	Propane, 1,1,1,2,3-pentachloro-2-methyl-	0 d	0 d	m.p. 20°	204/760	0.3	1
6589	Propene, 1,1,2,3-tetrachloro-3,3-difluoro-	2(16-35)26	2(19-36)28	1.4576	111/760	2.7	1
6001	Propionic acid, β -bromo-, methyl ester	0 d	0 d	1.4550	59/12.0	1	1
6037	Propionic acid, α -bromo-, β -methoxy-, methyl ester	0 d	0 d	1.4764	100/25.0	1	1
6309	1,3-Propanediol, bis(β -bromo-propionate)	2(51-122)87	2(14-53)24	1.4932	119/1.04	4.3	13
6068	Benzoic acid, 3-Chloropropyl ester	2(80-97)82	2(27-28)28	1.5221	105/1.0		13
6084	Benzoic acid, o-chloro-propyl ester	0 d	0 d	1.5160	93/1.0	1	13
6088	Benzoic acid, o-chloro-, isoamyl ester	5(15-192)87	5(18-53)33	1.5068	105/1.0		13
6085	Benzoic acid, m-chloro-, propyl ester	2(38-38)28	2(39-41)40	1.5138	89/1.0		13
6087	Benzoic acid, m-chloro-, butyl ester	2(6-49)28	2(9-17)13	1.5101	97/1.0		13
6090	Benzoic acid, m-chloro-, isoamyl ester	2(44-70)57	2(47-49)48	1.5056	105/1.0		13
6083	Benzoic acid, p-chloro-, ethyl ester	2 d	2 d	1.5207	78/1.0	1	13

RESTRICTED

RESTRICTED

74.

Orlando Number	Name	Repellent Time		N _D (22°)	b.p. °/mm.	Irrit. Exp. Index	Exp. Method
		Aedes	Anopheles				
6082	Benzoic acid, p-chloro-, propyl ester	0 d	0 d	1.5172	87/1.0	1	13
6086	Benzoic acid, p-chloro-, butyl ester	2(39-76)58	2(45-86)66	1.5129	99/1.0		13
6089	Benzoic acid, p-chloro- isoamyl ester	2(59-70)65	2(11-34)23	1.5082	104/1.0		13
6590	Coumarin, 6-chloro-, Sulfur	not tested		m.p. 161°		1.3	1
6557	1-Octanethiol	2(50-86)68	2(52-89)71	1.4509	146/760	4.7	1
6520	1-Decanethiol	2(71-159)115	2(47-47)47	1.4528	114/13	4.7	1
6624	Benzenesulfonic acid, methyl ester	2 d	0 d	1.4696	157/18	8.0	79
6586	Orthocarbonic acid, tetrathic-, tetramethyl ester	0 d	0 d	m.p. 65°	126/12	0.7	80
6574	Carbamic acid, diethyldithio-, carbomethoxymethyl ester	2(93-93)23	2(97-40)32	1.5089	100/0.4	1.7	30

RESTRICTED

75.

RESTRICTED

The Naval Medical Research Institute has reported the following average repellent times of several of our repellent compounds under sweating conditions (90° F. dry bulb, 80° F. wet bulb). Two tests were run in each case against *Aedes aegypti*.

Table VIII

Repellents under Sweating Conditions

Orlando Number	Name	Average Repellent Time	
		Sweating	Normal
6133	Cyclohexanecarboxylic acid, 1-hydroxy-, cyclopentyl ester	147	288
6154	1,5-Pentanediol, dipropionate	92	257
6168	Succinamic acid, N,N-diethyl-, propyl ester	84	396
6168-a	Succinamic acid, N,N-diethyl-, propyl ester	147	396
6216	Hydraacrylic acid, (3-phenyl-, ethyl ester	37	352
6216-a	Hydraacrylic acid, (3-phenyl-, ethyl ester	139	352
6252	Succinamic acid, N,N-dipropyl-, ethyl ester	162	260
6254	1,3-Cyclohexanediol, monopropionate	155	308

EXPERIMENTAL

The methods are recorded only in outline form; the exact equipment and technique used is omitted. The order of presentation is that occurring in Table VII. When compounds have been prepared by the same general procedure, they have been assigned identical preparation numbers. The equipment used was that ordinarily available in a well-equipped laboratory; the techniques employed were standard methods.

The large scale preparations were in general handled in several portions; the largest containers were a 12-l. flask and a 90-l. battery jar. References have been included with the descriptive material. Physical constants are reported in Table VII, and average yields are indicated in most cases.

1. These compounds were obtained from stock and judged to be sufficiently pure for testing.
2. These hydrocarbons were obtained as by-products in the reaction between benzylmagnesium chloride and formaldehyde (Tiffeneau, *Compt. Rendu*, **137**, 574 (1903); Gilman, *J. Am. Chem. Soc.*, **56**, 1127 (1934)). Bibenzyl was subsequently obtained from the Eastman Kodak Company.
3. 1,1-Diphenylethylene was prepared from phenylmagnesium bromide and ethyl acetate as described in "Organic Syntheses", John Wiley and Sons, N. Y. C. (1941), Coll. Vol. I, p. 226.
4. These alkyl hydrogen succinates and glutarates were prepared by heating the anhydride (1 mole) and the appropriate alcohol (1.2 moles) under reflux at a bath temperature 20-30° above the boiling of the alcohol. Heating was continued for twenty to thirty minutes after the refluxing had subsided and the product was then purified by distillation (yield 85-95 percent). A "Glascol" mantle was found to serve as a convenient heating unit, particularly in the large runs in which a 12-l. flask was used. In this case the course of the reaction was followed by placing a thermometer in the reaction mixture which should be occasionally shaken or stirred. It was found that a sufficiently pure product was obtained by merely removing the excess alcohol from the reaction mixture by distillation in vacuo.
5. The half esters of adipic acid were prepared from the diester, the acid, and the requisite alcohol according to the directions of "Organic Syntheses," John Wiley and Sons, N. Y. C. (1943), Coll. Vol. II, p. 276.
6. The alkyl hydrogen phthalates were prepared from the anhydride, the alcohol and pyridine by a modification of the procedure described in "Organic Reactions," Vol. II, 401 (1944) (cf. Goggans and Copenhagen, *J. Am. Chem. Soc.*, **61**, 2909 (1939)).

7. These compounds were prepared by adding the acyl chloride dropwise to a mixture of the appropriate hydroxy compound, some inert solvent such as benzene, ether or chloroform and sufficient pyridine to combine with the hydrogen chloride formed in the reaction (Blaise, Bull. Soc. Chim, (4), 15, 668 (1914)). In the case of glycol monoesters about 75 percent of the theoretical quantity of acid halide was used, the yields of monoester were 50-60 percent.

8. *o*-Ethoxybenzoic acid was prepared from the sodium salt of ethyl salicylate and ethyl iodide. The resultant ethyl ethoxybenzoate was saponified, the free acid being liberated by acidification.

9. The α -hydroxy acids were obtained by adding concentrated hydrochloric acid to a stirred, cooled mixture of ether, sodium cyanide and the requisite carbonyl compound at such a rate that the temperature did not rise above 0-5° C. The ether was removed and the cyanohydrin converted to the acid by heating with concentrated hydrochloric acid (Buchner, Ber., 27, 1231 (1896)).

10. These amide-acids were prepared in good yield by heating succinic anhydride with the appropriate amine in benzene for four hours. The acids crystallized from a mixture of benzene and medium-boiling petroleum ether, J. Organic Chem., 6, 774 (1941).

11. Glutaric anhydride was prepared from commercial dimethyl glutarate (du Pont); the ester was hydrolyzed by heating with concentrated hydrochloric acid, and the acid was converted to the anhydride by use of acetic anhydride. Twenty-one hundred grams (60% yield) of the anhydride was obtained from 4900 g. of ester (cf. Org. Syn., Coll. Vol. I, 91 (1941)).

12. These anhydrides were prepared from the proper acid and acetic anhydride as described in "Organic Syntheses," John Wiley and Sons, N. Y. C. (1941), Coll. Vol. I, p. 91.

13. These compounds were made by direct esterification using *p*-toluenesulfonic acid (2-4%) as catalyst. The acid (1 mole), carbinol (1.2-3 moles), catalyst and a suitable solvent such as benzene, toluene, petroleum ether or chloroform were heated under reflux. The water produced in the reaction was removed continually as formed by means of a Dean-Stark moisture trap.

14. The acid chloride was added to a mixture of magnesium, ether and the appropriate carbinol (Spasson, "Organic Syntheses," John Wiley and Sons, N. Y. C. (1940), Vol. 20, p. 21).

15. This methyl ester was made by direct esterification using concentrated sulfuric acid as catalyst (Purdie and Marshall, J. Chem. Soc. 59, 476 (1891)).

16. Several esters were prepared by treating an anhydride with the requisite alcohol in benzene. This procedure was necessary to avoid polymerization which occurred when direct esterification employing an acid catalyst was attempted.

17. These compounds were prepared by heating the glycol or amino-alcohol with the appropriate anhydride in toluene solution under reflux for several hours; the reaction was vigorously exothermic at reflux temperature.

18. These compounds were prepared by heating the glycol or aminoalcohol (1 mole) with 99% formic acid (2 moles) for several hours; the product was isolated by distillation. The yields were 50-95%.

19. A solution of the chloroformate and excess carbinol was boiled for several hours.

20. Phenol esters were prepared by adding the calculated amount of anhydride to a cooled, stirred solution of the phenol in aqueous potassium hydroxide (cf. Chattaway, J. Chem. Soc., 1931, 2495).

21. A suspension of the phosgene-pyridine complex in toluene was treated with an equivalent amount of the requisite phenol (Rabjohn, Org. Syn., to be published).

22. These compounds were obtained by transesterification using p-toluenesulfonic acid as the catalyst.

23. The γ -lactone of α -hydroxy- α -methylglutaric acid was prepared from levulinic acid and hydrogen cyanide by the method of Block Kreokler and Tollens, Ann., 238, 288 (1887). The propyl ester was prepared by direct esterification as described in Prep. Method 13.

24. This ester was prepared by heating the acid with methanolic hydrogen chloride.

25. These esters were obtained in good yield by treating a chloroform-ether solution of the alkyl hydrogen phthalate with diazomethane.

26. Furfuryl furoate was prepared by adding 2-furaldehyde to a boiling solution of sodium furfuryloxide, furfuryl alcohol and benzene (Neilson, J. Am. Chem. Soc., 66, 1230 (1944)).

27. Vanillic acid was prepared from vanillin through the oxime. The oxime was dehydrated with acetic anhydride and the resulting acetate of vanillonitrile was hydrolyzed (Raiford and Potter, J. Am. Chem. Soc. 55, 1683 (1933)). An attempt to prepare the acid by permanganate oxidation of vanillin was unsuccessful. The acid was esterified directly (Prep. Method 13).

28. These cyclic ketals, acetals and dioxolanones were prepared by heating a mixture of the carbonyl compound, the dihydroxy compound, benzene and a trace of p-toluenesulfonic acid as catalyst. The water produced in the reaction was removed continuously as formed by azeotropic distillation by means of a Dean-Stark moisture trap (Salmi and Pohjola, Ber., 72, 798 (1939)).

29. Concentrated sulfuric acid was added to a stirred and cooled mixture of the appropriate dihydroxy and carbonyl compounds (Konigsberger, Ber., 56, 2107 (1923)).

30. Sodium salts of the indicated acids were heated under reflux in alcohol solution with chloroacetone or methyl bromoacetate for several hours (Brewer and Zincke, Ber., 13, 635 (1880)). The yield was 50-60 percent.

31. These pyruvates were prepared by direct esterification as in Prep. Method 13 except that no catalyst was used.

32. These β -ketoesters were prepared by transesterification without a catalyst. The ethyl ester (1.5-2.0 moles) was heated with the requisite carbinol (1.0 mole) at 160° until the ethyl alcohol formed in the reaction had been completely removed. The product was then purified by fractional distillation at reduced pressure (Bacon, Am. Chem. J., 33, 79 (1905)).

33. Diethyl alkylidene-bis acetoacetates were prepared by condensing aldehydes with ethyl acetoacetate in the presence of pyridine. The crude bis-esters were then heated under reflux with acetic acid containing catalytic amounts of sulfuric acid. The resulting ethyl 6-alkyl-2-methyl-4-oxo-2-cyclohexene-1-carboxylates were obtained in 40-50 percent overall yields (Horning, Denekas and Field, J. Org. Chem., 9, 547 (1944)).

34. Diethyl diacetosuccinate was obtained by the condensation of sodioacetoacetic ester by means of iodine (Knorr, Ann., 306, 339 (1899)).

35. Diethyl γ -oxopimelate was prepared by the simultaneous hydration and esterification of 2-furanacrylic acid with ethanolic hydrogen chloride (Marokwald, Ber., 20, 2811 (1887)).

36. These compounds were prepared by direct esterification as described in Prep. Method 13 using a large excess of glycol.

37. These ethyl 2-alkyl-3-hydroxybutyrates were prepared by the hydrogenation of the corresponding acetoacetates over Raney nickel in alcohol at 125-150° C. (Adkins, Connor and Cramer, J. Am. Chem. Soc., 52, 5192 (1932)).

38. These β -hydroxyesters were prepared by the method of Reformatsky from the appropriate α -bromoesters and carbonyl compounds (Shriner, "Organic Reactions," John Wiley and Sons, N. Y. C. (1942), Vol. I, pp. 16, 17). Turnings of a copper-zinc alloy (92% Zn - 8% Cu) were used instead of the more customary forms of zinc.

39. This compound was prepared by heating propionic acid (0.25 mole), styrene oxide (0.30 mole) and benzene under reflux overnight. The unchanged acid was extracted with dilute sodium carbonate solution and the product purified by distillation. Yield 30%, Sapon. Equiv.: Calc'd 194, Found 203.

40. These glycol monoesters were prepared in 50-60 percent yields by adding about 75% of the theoretical quantity of anhydride to the glycol in toluene solution and bringing the mixture to a boil.

41. This glycol monoester prepared according to Method 7 was isolated by selective extraction. This procedure was required in order to free the product from diester, always a contaminant; distillation is not applicable because of similar boiling points. The monoester was freed from glycol by washing with a small amount of water and from diester by treating the residue with a large quantity of water, sufficient to dissolve the monoester, and then extracting the diester with ether. The monoester was recovered by saturating the aqueous solution with salt followed by chloroform extraction, yield 46%. Sapon-Equiv: Calc'd. 172; Found, 179, 181.

42. Propionyl chloride (1 mole) was added with stirring to a mixture of glycol (1 mole), pyridine (1.5 moles) and chloroform at 10°. The chloroform and pyridine were removed by distillation in vacuo. The residue was dissolved in chloroform and washed with dilute hydrochloric acid until acid to litmus and then with water until neutral. The chloroform was removed and the residue was extracted four or five times with equal volumes of low-boiling petroleum ether at -60°. Essentially pure monoester was obtained upon distillation of the residue. Selective extractions was necessary to separate the mono- from the diester as they boil at about the same temperature and fractional distillation is not applicable.

43. 1,4-Cyclohexanediol dipropionate was partially hydrolyzed with potassium hydroxide in 50 percent alcohol (37% yield). This procedure is based on that of Aldersley, Burkhardt, Gillam and Hindley, J. Chem. Soc., 1940, 10.

44. The appropriate chlorohydroxyester (prepared by application of Prep. Methods 9 and 13 to chloroacetone) was heated with freshly fused sodium acetate at 190-200°; the product was extracted with ether, washed and distilled. Yield 75 percent (Fournau and Tiffeneau, Bull. Soc. Chim., (4), 15, 22(1914)).

45. Commercial borneol (1 mole), ethyl orthoformate (2 moles) and a trace of p-toluenesulfonic acid were distilled at atmospheric pressure to yield the theoretical quantity of alcohol. The residue was distilled in vacuo without removal of the catalyst (55% yield).

46. A mixture of the appropriate ethyl orthoester (1 mole), carbinol (6 moles) and a trace of p-toluenesulfonic acid was heated until the theoretical quantity of alcohol had distilled. The residue was fractionally distilled in vacuo without removal of the catalyst. The yield was 60-85 percent.

47. To a solution of benzotrichloride in an equal volume of dry propanol at 100°, a solution of sodium propoxide (10% excess) in about 23 parts of propyl alcohol was added dropwise. The thick paste was diluted with benzene and filtered. The product was purified by distillation; yield 60 percent (cf. Post, "Chemistry of Aliphatic Orthoesters", Reinhold Publishing Co., N. Y. C. (1943), p. 17).

48. This compound was prepared by the action of alcoholic hydrogen chloride on acrolein; 25% yield (Fingert, Org. Syn., to be published).

49. These acetals or ketals were prepared by transacetalization. The acetal or ketal (1 mole), the hydroxy compound (2-3 moles) or carbonyl compound and a trace of p-toluenesulfonic acid were heated until a theoretical quantity of the replaced compound had distilled (80-90% yields).

50. These acetals were prepared by heating a mixture of the carbonyl compound, ethyl orthoformate, absolute alcohol and a trace of p-toluenesulfonic acid under reflux for 3 - 10 minutes and neutralizing the catalyst with calcium carbonate (Faulk, Ann., 389, 230 (1911)). The yields were 50-90 percent.

51. A mixture of styrene oxide (1 mole) and the carbinol (7 - 10 moles) in which a small amount of sodium had been dissolved were heated under reflux overnight. After washing, the product was purified by distillation (yield 60-80 percent) (cf. Emerson, J. Am. Chem. Soc., 67, 516 (1945)).

52. These compounds were prepared by the catalytic hydrogenation of 4-(2-furyl)-3-butene-2-one (Adkins and Burdick, J. Am. Chem. Soc., 56, 438 (1934)).

53. 4-(2-Furyl)-3-butene-2-one was prepared from acetone and 2-furaldehyde by a Claisen type condensation ("Organic Syntheses," John Wiley and Sons, N. Y. C. (1941), Coll. Vol. I, p. 283).

54. This acyloin was prepared by adding ethyl caproate to a stirred mixture of powdered sodium and absolute ether at such a rate that the mixture refluxed rapidly. This synthesis is based on the preparation of butyrolin as described in "Organic Syntheses," John Wiley and Sons, N. Y. C. (1943), Coll. Vol. II, p. 114. The yield was 50-60 percent.

55. These compounds were prepared by catalytic hydrogenation using Raney nickel at 125° and 1500 lbs. pressure (Adkins, "Reactions of Hydrogen", Wisconsin Press, (1937), p. 50).

56. These α,ω -glycols were prepared by hydrogenolysis of the corresponding diesters using copper-chromite catalyst (Adkins and Wojcik, J. Am. Chem. Soc., 55, 4939 (1933)).

57. 3,4-Diethyl-3,4-hexanediol was prepared from diethyl ketone by a bimolecular reduction ("Organic Syntheses," John Wiley and Sons, N. Y. C. (1941), Coll. Vol. I, p. 459).

58. N, N-Diethylbutyramide was prepared by heating methyl butyrate (40 g.) and diethylamine (30 g.) in a bomb at 200-210° for two days (Adkins, J. Am. Chem. Soc., 56, 2419 (1934)).

59. These N-substituted imides were prepared by adding the appropriate amine to a cold benzene solution of phthalic anhydride or succinic anhydride. The benzene was removed and the amide heated to 200° for thirty minutes to effect cyclization. The phthalimide was distilled under reduced pressure (70-75% yields).

60. Cyclohexene was slowly added to a stirred solution of peracetic acid in acetic acid (Scanlan and Swern, J. Am. Chem. Soc., 62, 2305 (1940)). The temperature spontaneously rose to 60° and the reaction mixture was heated for one-half hour more at 85°. After standing for sixty hours at room temperature the solution was warmed to 60-70° for one hour and poured into water. Sodium carbonate was added until the solution was alkaline, and the mixture was extracted with chloroform. After removal of the solvent, the product was distilled. The yield was 23 percent.

61. The ester-acid chloride (1 mole) (see below) was added dropwise over a period of several hours to a well-stirred mixture of the amine (2.2 moles) and approximately two volumes of dry ether at 0°. Ether and benzene were added to the reaction mixture which was then washed with dilute acid, dilute sodium carbonate solution and cold brine. After drying over anhydrous magnesium sulfate and removal of the solvent, the product was distilled. Occasionally the product was contaminated with a small amount of a white solid which came over in the early part of the distillation and appeared to be the amine hydrochloride. This was removed by filtration. The yield was 70 to 85 percent.

Several succinamates were originally prepared by direct esterification of the corresponding succinamic acid (Prep. Method 10); however, the yields were very poor, probably due to alcoholysis of the amide group, and a better method was sought. This consisted in preparing the half-ester of the appropriate acid (Prep. Method 4), converting it to an ester-acid chloride and condensing the acid chloride with an amine. The ester-acid chloride were conveniently prepared by adding phosphorus pentachloride (1.02 moles) with occasional swirling over a period of 10 - 30 minutes to the ester acid (1 mole). This operation was carried out in a hood. The phosphorus oxychloride formed in the reaction was then removed by distillation in vacuo; the bath temperature not being allowed to rise above 80°. The crude acid chloride was used without further purification. In the case of mono-sec-butyl succinate the product decomposed when phosphorus pentachloride was added and thionyl chloride (2 moles) was used instead. The use of thionyl chloride was in general avoided as the final product (amide-ester) occasionally had an objectionable odor, although it possessed the same refractive index as material prepared by use of phosphorus pentachloride.

62. The ester-acid chloride (1 mole) was added dropwise at a rate such that the temperature did not rise above 5° to a well-stirred mixture of the amine (1.2 moles), 20-25 percent potassium hydroxide solution (1 mole) and some ether at 0°. The layers were separated, the aqueous part extracted once with ether and the combined ethereal portions were washed with dilute acid, dilute alkali and cold brine. After drying over anhydrous magnesium sulfate and removal of the solvent, the product was distilled. Yield 60 to 85 percent of theory. As in Prep. method 61 a white solid occasionally came over in the early part of the distillation.

63. Ethyl hydrogen Maleate (geometric configuration not certain) was prepared by the method of Shields (J. Chem. Soc., 59, 740 (1891)). The maleamic acids were then prepared as described in Prep. Method 61. Ethyl hydrogen maleate proved to be very unstable when efforts were made to prepare it according to the directions in Prep. Method 4. When the product obtained by warming maleic anhydride (1 mole) and ethyl alcohol (1 mole) was directly treated with phosphorus pentachloride (1 mole) and the amide prepared immediately according to Prep. Method 61, variable results were obtained. In one case the yield was 70 percent.

64. These compounds were prepared by heating a mixture of potassium succinimide, the proper haloester and butanol (Clemo and Ramage, J. Chem. Soc. 1931, 49). The yield was 69 percent.

65. The γ -lactone of α -hydroxy- α -methylglutaric acid (Prep. Method 23) was converted to the acid chloride with phosphorus pentachloride. The acid chloride was then condensed with the appropriate amine (Prep. Method 61). The yield was 60-70 percent.

66. Molar quantities of primary alkyl amine and β -keto diester were allowed to stand with a small amount of methanol for three days; the aqueous layer was separated and the product distilled. The yields varied from 60 to 80 percent (Sauer and Adkins, J. Am. Chem. Soc., 60, 406 (1938)).

67. These compounds were made from the appropriate amines and chloroformates essentially as described in Prep. Method 62. The yield was 85 percent.

68. The necessary sodium alkoxide in an excess of the alcohol was added gradually to a molar quantity of α -chloro-N,N-diethylacetamide (see below). In the case of α -cyclohexoxy-N,N-diethylacetamide dioxane was used as a solvent; the yields were 64-67%. The procedure is based on that of Pratt and Robinson, J. Chem. Soc., 1925, 168.

α -halo-N,N-dialkylacetamides were prepared in 70 to 80 percent yield by adding the amine (1 mole) slowly to a well-stirred solution of the haloacid halide (1 mole) in absolute ether at -20 to -10° .

69. Diketene was added to the indicated amine in aqueous solution or suspension at $C - 20^\circ$ (80-90% yields) (Boese, Ind. Eng. Chem., 32, 16 (1940)). Diketene was prepared by passing acetone over a hot filament (Hurd, "Organic Syntheses," John Wiley and Sons, N. Y. C. (1941), Vol. 21, p. 64) and allowing the ketene to dimerize.

70. Levulinyl chloride was prepared in 55 percent yield by the action of thionyl chloride on the acid in chloroform at 0° (Clemo and Ramage, J. Chem. Soc., 1931, 54). The amides were prepared from the acid chloride and excess amine as in Prep. Method 61.

71. N,N-Dipropyllevulinamide (Prep. Method 70) was reduced with aluminum isopropoxide in isopropanol by standard procedures (95 percent Yield) (Wills, "Organic Reactions," John Wiley and Sons, N.Y.C. (1944), Vol. 2, p. 203).

72. These β -hydroxyamides were prepared in 34 to 62% yields from the appropriate carbonyl compounds and α -halo-N,N-dialkylacetamides (Prep. Method 68) by standard Reformatsky procedures (Prep. Method 38). As was expected the bromoamides gave more satisfactory results than the corresponding chloroamides. Because the use of bromoamides in the Reformatsky type reaction is not mentioned in the latest review which has come to our attention (Shriner, "Organic Reactions," Vol. I, p. 17, John Wiley and Sons, N. Y. C. (1942)) the following hydroxyamides were redistilled and submitted for analysis (Miss E. Werble, this laboratory):

Valeramide, 3-hydroxy-3-methyl-N,N-dipropyl-

Calcd for $C_{12}H_{25}NO_2$: C, 66.98; H, 11.6

Found: C, 66.26; H, 11.4
66.17 11.5

Caproamide, N,N-diethyl-3-hydroxy-3-methyl-

Calcd for $C_{11}H_{23}NO_2$: C, 65.67; H, 11.4

Found: C, 64.91; H, 10.9
64.81 11.0

Cyclohexanecetamide, N,N-diethyl-1-hydroxy-

Calcd for $C_{12}H_{23}NO_2$: C, 67.57; H, 10.37; N, 6.57

Found: C, 66.34; H, 10.40; N, 6.53
66.94 10.55 6.60

Cyclohexanecetamide, 1-hydroxy-N,N-diisopropyl-

Calcd for $C_{14}H_{27}NO_2$: C, 69.71; H, 11.2

Found: C, 69.43; H, 10.8
69.43 10.8

Hydracrylamide, N,N-diethyl- β -phenyl-

Calcd for $C_{14}H_{19}NO_2$: C, 70.59; H, 8.60

Found: C, 69.29; H, 8.16
69.35 7.73

73. These N,N-disubstituted glycine esters were prepared by adding the requisite bromoester to two moles of the secondary amine at 0° (30% yields) (V. Braun, Ber., 40, 3941 (1907)).

74. This group of substituted glycine esters was prepared by adding the indicated primary amine to one mole of the necessary bromoester at 0° (Alpern and Weizmann, J. Chem. Soc., 1911, 86). The yields were 30-40 percent.

75. The appropriate hydroxyamine was refluxed with sodium chloroacetate in aqueous solution for seven hours. After removal of the water by distillation in vacuo the residue was distilled (60% yield) (Chem. Abs., 34, 1023 (1940)).

76. These aminoesters were prepared by treating the potassium derivatives of pyrrole with the proper bromoester as described by Sohl and Shriner (J. Am. Chem. Soc., 53, 4168 (1931)). The yields were 25-45%.

77. Phenylethylene oxide was heated under reflux with a slight excess of the appropriate amine (Emerson, J. Am. Chem. Soc., 67, 516 (1945)).

78. This oxime (Kling, Ann. Chim. Phys., (8), 5, 481 (1905)) was prepared in 80 percent yield from acetal acetate by the method of Huckel and Loehs (Ann., 498, 162 (1932)). The product was extracted with ether and distilled.

79. Benzenesulfonyl chloride was treated with methanol and alkali according to standard procedure; the yield was about 50 percent.

80. Tetramethyl tetrathioorthocarbonate was prepared from S-methylisothioureia sulfate according to the directions of Baeker and Stedhouder (Rec. Trav. Chim., 52, 926 (1933)).

81. This orthocarbonate was made by the action of chloropierin on sodium 2-methoxyethoxide (38% yield) (Bartel, Ber., 60, 1841 (1927)).

APPENDIX

Prepared by W. J. Shenk, Jr.

A statistical analysis by functional groups of all the compounds in our card index as of February 15, 1945, which have average repellency times of better than 180 minutes (or ten days in the case of cloth test) to the first bite against *Aedes aegypti* or 120 minutes against *Anopheles quadrimaculatus* has been made. The compounds which meet the above requirements are hereinafter referred to simply as repellent compounds, all others being classed as non-repellent. All of the esters of Group IV of the classification system were similarly analyzed.

The analyses have the weaknesses of statistical analyses in general but we believe that when completed they will give an illuminating survey of the types of compounds tried and not tried and of the chances of obtaining a repellent by making a certain type of compound.

Analysis of Repellent Compounds:

The repellent compounds were extracted from our card index of the testing results obtained at Orlando. As in the card index, the compounds were separated according to molecular structure into the ten chief groups listed in the left hand column of Table IX. It is important to note that in classifying poly functional compounds the following order of group preference was arbitrarily assigned: X, VIII, IX, I, II, III, IV, V, VI, VII. Thus an amide-ester is in group VIII-a and not group IV. The compounds in each chief group were then analyzed for the following functional groups; cyclo (any cyclic structure), hydroxyl, ether, ester and ketone. The results of the above analysis are summarized in Table IX.

The first column of figures in Table IX gives the number of repellent compounds in the chief groups; the total number is 227. The columns of figures under the headings cyclo, hydroxyl, ether, ester and ketone give the number of compounds in the chief group which contain one or more of the indicated functional groups. It is to be noted that when the column heading is the same functional group as that of the chief group, the figure given indicates the number of compounds containing two or more of such groups. Thus, if Group V (ethers) is under consideration, the figures reading from left to right denote that of the 44 repellent ethers 37 contain one or more cyclo groups, 30 one or more hydroxyl groups, 17 two or more ether groups and 6 one or more ketone groups. The blank in the ester column arises from the fact that ether-esters are classified in Group IV (esters) in accordance with the order of preference rule.

The columns are then summed up, but in order to obtain the total number of compounds containing one or more functional groups of a given kind, the number of compounds in the chief functional groups which were not included in the column must be added. Thus to obtain the total number of repellent compounds which contain one or more ether groups, 27 must be added to the total of 63 at the bottom of the ether column, because only 17 of the 44 Group V ethers are represented in this column.

Table IX

Chief Group	No. Present	Functional Groups				Number of Groups Present			Av. Mol. Wt.	Mol. wt. Range
		Cyclo	Hydroxyl	Ether	Ester	Keto	3 or more	two one		
I. Hydrocarbons	0	0	0	0	0	0	0	0		
II. Acids	9	0	1	0	1	0	0	0		
III. Aldehydes	10	10	0	8	0	0	0	0	154	90-195
IV. Esters	70	57	27	21	13	3	58	11	168	148-202
V. Ethers	44	37	30	17		6	43	1	206	145-284
VI. Ketones	3	2	1			0	1	0	184	130-255
VII. Carbinols	21	17	6			0	10	0	183	174-200
VIII-a. Amides	24	13	0	3	3	0	3	0	159	104-204
VIII-b. Amines	15	13	4	2	9	0	15	7	190	115-233
VIII-c,d. Nitrogen	9	7	0	4	4	0	8	0	190	119-281
IX. Halogen	16	13	10	6	4	2	16	0	181	143-213
X. Sulfur and Phosphorus	6	1	0	2	1	0	2	1	197	143-274
									192	150-234

Total

227	170	79	63	35	11	164	47	16	182	90-284
	+0	+15	+27	+57	+3					

Overall Total

227	170	94	90	92	14	164	47	16		
-----	-----	----	----	----	----	-----	----	----	--	--

Percentage of 227

75%	41%	40%	41%	6%	72%	21%	7%			
-----	-----	-----	-----	----	-----	-----	----	--	--	--

Under the heading of Number of Groups Present, the number of compounds in each chief group having a total irrespective of kind of one, two, or three or more functional groups is tabulated. In the three or more classification the great majority have three functional groups. The last two columns record the average molecular weight and the molecular weight range of each of the chief groups respectively. It is to be noted that the molecular weight range is considerably shortened when the middle ninety percent of the compounds in a chief group are considered. Thus, the range of Group IV is shortened from 145-284 to 175-245.

In the last row the fractions of the 227 repellent compounds having the indicated properties are listed in percents. However, in order to evaluate these findings it is necessary to make a comparison between the repellent and the corresponding non-repellent compounds, that is to say to determine what percentage of the non-repellent compounds have cyclo groups etc. As a start such a comparison was made in the case of Group IV esters.

Analysis of Group IV:

A total of 763 Group IV esters have been tested; of these, 70 or 9.2 percent are repellent.

Of the 70 repellent esters 64 or 92 percent fall in the molecular weight range 175-249, whereas only 399 or 52 percent of all esters tried fall in this range.

Or looking at it another way, of the 399 esters in the molecular weight range 175-249, 64 or 16 percent are repellent. Thus by limiting molecular weight to a range of 175-249 the chances of making a repellent ester will be increased from 9.2 to 16 percent or by 75 percent. Therefore, molecular weight⁺ is important.

Group IV Esters in the Molecular Weight Range 175-249

A comparison between repellent and non-repellent esters with molecular weights in the range 175-249 is presented in Table X. The first column of figures gives the number of repellent and non-repellent esters in Group IV which fall in the molecular weight range of 175-249 and finally at the bottom the percentage of the total number tested which are repellent. The next seven columns tabulate the numbers and percentages of the repellent and non-repellent compounds which contain one or more of the indicated groups with the exception of the ester column which denotes diesters. The last three columns give the numbers of repellent and non-repellent compounds which contain one, two, or three or more functional groups.

⁺Actually we believe that the vapor pressure of the compound at 37° C. is the important factor and have merely used molecular weight by way of a crude approximation of vapor pressure.

Table I

Comparison of Repellent and Non-repellent Group IV Esters having molecular weights in the range 175-249

	Number Present	Non-				No. of Functional Groups			
		Cyclo	Cyclo	Hydroxy	Phenolic	Ether	Ester	Keto	I II III
Repellent	64	54	10	25	0	21	10	3	1 7 56
Percent of Total Repellent		84	16	39	0	33	16	47	1.6 11 87.4
Non-Repellent	335	187	146	33	18	74	114	28	33 142 160
Percent of Total Non-repellent		56	44	10	5.4	22	34	8.4	10 42 48
Total Esters	399	241	158	58	18	95	124	31	34 149 216
Percent of Total Esters		60	40	14.5	4.5	24	31	7.8	8.5 37 54

RESTRICTED

Percent Repellent of Total Tested	16%	22%	6.3%	42%	0%	22%	8%	10%	3%	4.7%	26%
-----------------------------------	-----	-----	------	-----	----	-----	----	-----	----	------	-----

90.

RESTRICTED

By comparing the various percentages in the bottom row with the 16 percent average value, it can be seen that the presence of cyelo, hydroxyl, and ether groups enhances the chances that a Group IV ester candidate will be repellent. It can be further seen that the presence of a second ester group halves the chances of obtaining a repellent. Of particular significance is the fact that 56 or 87.4 percent of the repellent esters in Group IV which fall in the molecular weight range 175-249 possess three or more functional groups, whereas only 216 or 54 percent of all esters in this category have this number. Also of the 216 esters containing three or more groups 56 or 26 percent are repellent. Thus by choosing only esters which have molecular weights in the range 175-249 and possess three or more functional groups, the chances that a candidate ester will be repellent have increased from 9.2 to 26 percent, an increase of 138 percent. The importance of the presence of three or more functional groups is further emphasized by the fact that only 4.7 percent of the difunctional compounds tried were repellent.

Group IV Esters in the Molecular Weight Range 175-249
and Possessing Three or More Functional Groups:

A comparison between the repellent and the non-repellent esters which have molecular weights in the range 175-249 and contain three or more functional groups is presented in Table XI. This table was compiled in fashion similar to that described for Table X.

By comparing the various percentages in the bottom row with the 26 percent average for all compounds in this category the striking effect of the presence of a hydroxyl can be seen, for it has increased the chance that a candidate will be a repellent from 26 to 56 percent or by 115 percent. However, enough compounds of this type have not been tried to make the result statistically significant.

Because of the unusual showing of the hydroxyl group in Table XI a comparison between repellent and non-repellent hydroxy-esters in the molecular weight range 175-249 was made and is presented in Table XII. This table was again compiled in fashion similar to that described for Table X.

In Table XII it is noted that the hydroxyl group has a marked effect on repellency, particularly in cyclic compounds; however, in conjunction with an ester group alone it is insufficient.

In general it is concluded that in selecting a candidate ester, the ester should have a molecular weight between 175-249 (preferably a boiling point between 80 and 120° C. at 0.5 mm.) and that it should contain three or more functional groups. Of these groups the hydroxyl, cyelo, and ether groups, in that order, are noticeably beneficial whereas the presence of a second ester group is definitely detrimental. Enough keto-esters have not been prepared to warrant any conclusions with regard to them. Again it is to be emphasized that these conclusions are the

Table XI

Comparison of Repellent and Non-Repellent Group IV Esters in the Molecular Weight Range 175-249 and having three or more Functional Groups

	No.	Present	Non-cyclo	Cyclo	Hydroxyl	Phenolic	Ether	Ester	Keto
Repellent	56	8	48	25	0	21	9	3	
Percent of total repellent		13	87	45	0	38	16	5.4	
Non-repellent	160	29	131	20	18	67	53	20	
Percent of total non-repellent		18	82	17.5	11	42	33	12.5	
Total Esters	216	37	179	45	18	88	62	23	
Percent of total esters		17	83	21	8.3	40	29	10.6	
Percent Repellent of Total	26	22	27	56	0	24	14.5	13	

Table XII

Comparison of Repellent and Non-Repellent Hydroxy-Esters in the
Molecular Weight Range 175-249

	No.	Cyclo	Non-cyclo	Ether	Ester	Keto	Hydroxyl	II	III	No. of groups present
Repellent	25	22	3	2	1	0	0	0	25	
Percent of total repellent		88	12	8	4	0	0	0	100	
Non-repellent	33	14	19	4	2	0	3	13	20	
Percent of total non-repellent		42	58	12	6	0	10	39	61	
Total	58	36	22	6	3	0	3	13	45	
Percent of total		62	38	10	5	0	5	22.4	77.6	
Percent Repellent of total tested	42	61	8	33	33	0	0	0	55.5	

RESTRICTED

RESTRICTED

REEL - C

1 3 1 7

A.T.I.

3 0 6 3 9

(23) * Insecticides

RESTRICTED

TITLE: The Preparation of Some Compounds for Testing as Insect Repellents

AUTHOR(S): Drake, Nathan L.; Baker, Charles M.; Kilmer, Glen W.; and others

ORIGINATING AGENCY: University of Maryland

PUBLISHED BY: Office of Scientific Research and Development, NDRC, Div. 9

ATI- 30639

REVISION (None)

ORIG. AGENCY NO
(None)

PUBLISHING AGENCY NO.
OSRD-P-6485

U

DATE	DOC. CLASS.	COUNTRY	LANGUAGE	PAGES	ILLUSTRATIONS
Dec '45	Repts.	U.S.	Eng.	93	tables

ABSTRACT:

EO 12501 dd 5 NOV 1953

This report contains the performance results of 631 organic compounds, mixtures and creams which were tested as insect repellents. Among the promising insect repellents tested after application to skin, 0-6133, 0-6154, 0-6168, 0-6216, 0-6290, and 0-6252 have passed acute toxicity tests and have been submitted for 90 day subacute toxicity studies. 0-6109, 0-6152, 0-6217, 0-6226, 0-6254 and 0-6263 have passed acute toxicity tests with some reservation and were not submitted to subacute toxicity studies. Results have led to the conclusion that in selecting a candidate repellent consideration should be given to boiling point and functionality. In general a candidate should have a boiling point in the range of 90-130°/0.5 mm and should be polyfunctional. 54% of the candidates submitted with regard to these criteria were repellent.

DISTRIBUTION: Copies of this report obtainable from Air Documents Division; Attn: MCIDXD

DIVISION: Materials (8) 14
SECTION: Misc. Non-Metallic Materials (8) 6

SUBJECT HEADINGS: Insecticides - Effectiveness (51956)

ATI SHEET NO.: R-8-8-9

Air Documents Division, Intelligence Department
Air Materiel Command

AIR TECHNICAL INDEX

RESTRICTED

Wright-Patterson Air Force Base
Dayton, Ohio

P7/3 219500