REFERENCES

1. Silverstone, G., JAOCS 44:502 (1967).
2. Achaya, K.T., Ibid. 48:758 (1971).
3. Body, D.R., and F.B. Shorland, Ibid. 42:5 (1965).
4. Hawke, F., and E.A. Kohll, J. South Afr. Chem. Inst. 12:1,17 (1959).
5. Modak, S.N., and J.G. Kane, JAOCS 42:428 (1965).
6. Formo, M.W., in Bailey's Industrial Oil and Fat Products, Vol. 1, 4th Edn., edited by D. Swern, John Wiley and Sons, New York, NY, 1979, p. 738.
7. von Mikusch, J.D., JAOCS 29:114 (1952).
8. Subbarao, R., Y.S.R. Sastry, V. Kale, H.S. Vedanayagam, T.C. Rao and G.Lakshminarayana, Paper 619, presented at the International Congress on Oilseeds and Oils, Oil Technologists' Association of India, New Delhi, Feb. 9-13, 1979.
9. Official and Tentative Methods of the American Oil Chemists' Society, 3rd Edn., 1958 (revised 1973), AOCS, Champaign, IL.
10. Achaya, K.T., B.M. Craig and C.G. Youngs, JAOCS 41:783 (1964).
11. Strocchi, A., and M. Piretti, J. Chromatogr. 36:181 (1968).
12. Mikolajczak, K.L., and M.O. Bagby, JAOCS 42:43 (1965).
13. Youngs, C.G., Ibid. 38:62 (1961).
14. Chipault, J.R., and J.M. Hawkins, Ibid. 36:535 (1959).

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Sodium Santalbate-Dimethyl Sulfate Inclusion Complex

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ABSTRACT

A molecular inclusion complex has been obtained from the major acetylenic acid, santalbic acid (octadec-11-en-9-ynoic acid or *trans*-11-octadecen-9-ynoic acid) of the seed oil of *Santalum album* L. by a simple treatment of its sodium salt with dimethyl sulfate. Aqueous solutions (0.5-1%) of the complex produce good lather and have efficient cleansing (detergent) action on grease and dirt particles.

INTRODUCTION

The seed oil of *Santalum album* L. is a drying oil obtained in about 55-60% yield by hot petrol extraction (1). The chemical aspects of the oil have been extensively studied earlier by many workers (2-4). The viscous oil contains 88% of santalbic glyceride and, by chromatography of the mixed fatty acids, about 60% of santalbic acid could be obtained.

The chemical reaction involving dimethyl sulfate and the sodium salt of a carboxylic acid is normally expected to give the methyl ester of the acid (5,6). It is also known that alkyl sulfates are of interest as sulfating and sulfonating reagents (7). But, in the case of sodium santalbate, the reaction with dimethyl sulfate furnished a molecular inclusion complex that had cleansing action on greasy and dirty particles.

EXPERIMENTAL PROCEDURES

Isolation of Santalbic Acid

The seed oil (50 g) was saponified by boiling with ethanolic potassium hydroxide (10 g in 200 mL) for 1 hr. Alcohol was distilled off and the solution was acidified; the mixed fatty acids (42 g) were extracted with ether. After the removal of solvent, the acids were passed through a silica gel (1:30) column with benzene as eluent (1,500 mL). The benzene eluate (37 g) was chilled in 200 mL of petroleum ether (boiling range 60-80 C) overnight at -10 C, when shining white plates of santalbic acid (mp 38-39 C) separated out (30 g, yield 60%).

Alternatively, santalbic acid may also be obtained by direct chilling of mixed fatty acids in petroleum ether or by direct treatment of crushed sandal seeds with alcoholic potash, followed by ether extraction of acids and chilling the ether solubles in petroleum ether. But, the yields by these methods are only 50 and 40%, respectively (8).

Preparation of Complex

Santalbic acid (10 g) was boiled with ethanolic sodium hydroxide solution (2.5 g in 100 mL) for 10 min. Alcohol was distilled off under vacuum, when a white solid mass of sodium santalbate was obtained, to which was added 3.5 mL of freshly distilled dimethyl sulfate (bp 186 C). The reaction, which was exothermic, was set aside for 30 min and then heated on a boiling water bath for 45 min with occasional swirling. A pasty mass was formed, which gradually solidified. Volatile material, if any, was removed under vacuum (15 mm Torr). The product was crushed into powder, washed with acetone (5 × 40 mL) and finally dried under suction, when a pale yellow amorphous powder (12 g) was obtained: IR $\gamma_{\max}^{\text{Nujol}}$ cm^{-1}: 2925-2800 (C-H), 1640 (conjugated C=C), 1560 $(\text{-C-}\underset{\underset{\text{O}}{\|}}{\text{O}}^{-})$, 1450, 1380, 1250-1220 (S=O), 1070, 1000 (C-O), 950 (=C-H), 770 (S-O), 720.

The complex gave a positive Lassaigne's test for elemental sulfur and, upon burning, it gave a sooty flame, leaving aside a black residue. A 0.5-1% aq solution of the complex was found to give good lather and had cleansing action on dirty and greasy materials.

Hydrolysis with Acid

The complex (3 g) was added to 100 mL of 6 N HCl. The mixture was heated on a boiling water bath for 3 hr. The solution was cooled and then extracted with 3 × 100 mL of ether. The ether-soluble matter (2.1 g) was chilled in petroleum ether overnight at -10 C. The white solid (1.4 g) was filtered off and was identified as santalbic acid by mp, mmp, Co-TLC and Co-IR.

Hydrolysis with Aqueous Acetone

The complex (5 g) was refluxed with aq acetone (150 mL, 0.5%) for 10 hr. The acetone was distilled off and the product was dissolved in 100 mL of distilled water, then extracted with ethyl acetate (3 × 75 mL). The ethyl acetate-soluble matter (0.4 g) gave santalbic acid (0.23 g) upon chilling with petroleum ether.

Alkylation of Phthalic Anhydride

A mixture of the complex (10 g) and phthalic anhydride (3.6 g) was heated to reflux with sodium-dry benzene

(200 mL) for 6 hr under anhydrous conditions. The reaction mixture was cooled and the solid matter (6.5 g, white powder, sulfur test positive, no lather with water) was filtered off and washed with 3 × 30 mL of benzene. The benzene was distilled off and the crude residue (7.2 g) was chromatographed on silica gel (1:30) with benzene and ether as eluants. The benzene eluate (6.1 g), upon chilling with petroleum ether, gave santalbic acid (4.7 g). The ether eluate (0.8 g) was a reddish-yellow liquid, found to be a mixture of mono- and dimethyl phthalate, as confirmed by Co-TLC and Co-IR.

RESULTS AND DISCUSSION

Methylation of phthalic anhydride using the sodium santalbate-dimethyl sulfate complex in benzene medium and yielding a mixture of dimethyl and monomethyl phthalate, suggests that the dimethyl sulfate, which is physically adsorbed in the complex with sodium santalbate, is released by heat. Further evidence regarding the physical adsorption of dimethyl sulfate on sodium santalbate is provided by the IR spectrum of the complex, with the characteristic frequencies for $-\underset{\underset{O}{\|}}{C}-O^-$ at 1560 cm^{-1}, S=O at 1250-1220 cm^{-1}, C-O at 1000 cm^{-1} and S-O at 770 cm^{-1}. This paper is only intended to report that the normal reaction product between the salt of an acetylenic acid and a methylating reagent like dimethyl sulfate is not the methyl ester, but a molecular inclusion complex, hitherto unknown as far as sodium santalbate and dimethyl sulfate are concerned, and that the complex has a demonstrative cleansing property.

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REFERENCES

1. Shankara Narayana, K.H., J. Oil Technol. Assoc. India 11:96 (1979).
2. Morris, L.J., and M.O. Marshall, Chem. Ind. 460 (1966).
3. Hopkins, C.Y., M.J. Chisholm and W.J. Cody, Phytochemistry 8:161 (1969).
4. Hatt, H.H., A.C.K. Triffett and P.L. Wailes Aust. J. Chem. 12:190 (1959).
5. Preparative Organic Chemistry, edited by C. Hilgetag and A. Martini, John Wiley and Sons, New York, NY, 1972, p. 373.
6. Comprehensive Organic Chemistry, Vol. 3, edited by D.N. Jones, Pergamon Press, Oxford, 1979, p. 371.
7. Gilbert, E.E., Sulfonation and Related Reactions, (Interscience monographs on chemistry) John Wiley & Sons, New York, NY, 1965, p. 23.
8. Gunstone, F.D., and W.C. Russell, J. Chem. Soc. 3782 (1955).

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Extraction of Alkaloids and Oil from Bitter Lupin Seed

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ABSTRACT

Quinolizidine alkaloids and the oil were recovered from seeds of bitter lupin, *Lupinus mutabilis*, by 2 extractions using hexane as the only organic solvent. Ground and flaked lupin seed was extracted first with hexane, which recovers the oil and those alkaloids that occur as free bases. Subsequently, the hexane-insoluble salts of the alkaloids retained in the defatted flakes were converted into hexane-soluble free bases by treatment with aq sodium carbonate or ammonium hydroxide and removed by another extraction with hexane. A low-alkaloid proteinaceous meal was obtained with practically no loss of protein. The alkaloids dissolved in the oil were completely recovered by extraction with aq hydrochloric acid.

INTRODUCTION

The lupin, a leguminous plant, has great potential as an oilseed crop in regions having a temperate climate (1,2). The seeds of bitter lupin, *Lupinus mutabilis*, a variety widely cultivated in the Andean regions of South America, constitute a rich source of edible oil and protein (3). The use of products from bitter lupin seed in food and animal feed is restricted, largely due to the occurrence of toxic quinolizidine alkaloids (1). Breeding of *L. mutabilis* for the production of low-alkaloid, "sweet" lupin seed is still at an experimental stage (4).

Currently, the bitter lupin seed is processed in a manner similar to other oilseeds (2), i.e., the crushed and flaked seeds are extracted with hexane to yield the oil and a minor portion of the alkaloids. An edible oil is then obtained by refining, which leads to a complete removal of the alkaloids. The defatted lupin meal containing a major portion of the alkaloids must be "detoxified" prior to use in food and feed.

Blaicher et al. have shown recently that protein concentrates, virtually devoid of alkaloids, can be prepared from hexane-defatted meal of bitter lupin seed by extraction with aq alcohols (5). Although such protein concentrates should be eminently suitable for dietary supplement of an undernourished population, the production of these concentrates involves rather sophisticated technology that deviates considerably from the conventional processing of oilseeds. Thus, the use of 2 different solvents, i.e., hexane for defatting and aq alcohol for the removal of alkaloids and soluble carbohydrates, requires additional, elaborate equipment for solvent recovery.

In this work, we have explored the possibility of recovering alkaloids and oil from bitter lupin seed by extraction with hexane as the sole organic solvent. Our aim was to find a process that can be easily adapted to the existing technology of oilseed extraction to produce an edible oil and a low-alkaloid proteinaceous meal.

EXPERIMENTAL PROCEDURES

Material

Seeds of bitter lupin, grown in Chile, were crushed and flaked in a pilot plant as described elsewhere (5,6).

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